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THAMES HOUSE MILLBANK LONDON SW1

Telephone: VICtoria 3888

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INDEX

Properties of Mar-Ageing 18 Per Cent. Nickel-Cobalt-Molybdenum Steel *Pages* 115-6

Nickel Page

Determination of Trace Amounts of Cobalt in Nickel 117
Nickel Complex Analogous to Cobalt Carbonyl 117

Electrodeposition and Other Coating Methods

Corrosion of Decorative Nickel/Chromium Coatings 117
Electrodeposition of Nickel-Copper Alloys from the Pyrophosphate Solution 118
Electrodeposition of Nickel-Tungsten Alloys from the Pyrophosphate Solution 119
Purpose, Theory and Application of Nickel Dip in the Enamelling Industry 119

Non-Ferrous Alloys

Chromium and Nickel Solvuses in the Chromium-Nickel System 120
Influence of Metal/Mould Reaction and Section Thickness on the Properties of Nickel-containing Gunmetal Castings 120
Use of Cupro-Nickel for Fin Drums Drying Calcium-Carbonate Paste 121

Cast Iron

Use of 'Ni-Hard' in Crushing and Grinding Plant 122

Constructional Steels

Structure of Bainite in Hypoeutectoid Steels 122
Properties of Nickel-Aluminium Age-Hardening Nitriding Steel 122

Heat- and Corrosion-Resisting Materials Page

Investment Castings in High-Alloy Steels and Nickel- and Cobalt-base Alloys: British Standard 124
Intragranular Precipitation of Intermetallic Compounds in Nickel-containing Austenitic Alloys 124
Study of Carbides Present in 'Waspaloy' 125
Diffusion of Brazing-Alloy Constituents into Heat-Resisting Materials 125
Resistance of Nickel-containing Alloys and Steels to Thermal Fatigue 126
Properties of Stainless-Steel Sandwich Structures 128
'RA-333': High-Temperature Alloy Suitable for Critical Parts in Heat-Treating Furnaces 128
Nickel-containing Spring Alloys for Special Applications 128
Experience in Forging 'Astroloy' 129
Stainless-Steel Production in 1960 130
Experience in the Continuous Casting of Stainless Steel 130
Morphology of Martensite in Nickel-containing Steels 130
1st International Congress on Metallic Corrosion 130
Influence of Alloying Additions on the Electrochemical Behaviour of Stainless Steels 137
Corrosion Experience with Nickel-containing Materials in a Nitric-Acid Concentrator 137
Catastrophic Oxidation of Exhaust-Valve Stainless Steels in the Presence of Lead Oxide 138
Hydrogen Pick-Up During Aqueous Corrosion of Nickel-containing Zirconium Alloys 139
Heat-Treating of Stainless Steels in Protective Atmospheres 139
Welding and Heat Treating a 60-ton Stainless Steel Cryogenic Vessel 139
Arc-Welding of 'Inconel' for Nuclear Power Applications 139

Analysis 139

PROPERTIES OF MAR-AGEING 18 PER CENT. NICKEL-COBALT-MOLYBDENUM STEEL

INFORMATION is now available on the properties of a new 18 per cent. nickel-cobalt-molybdenum 'mar-ageing' steel developed by The International Nickel Company, Inc. The steel is unique, in that it is capable of exhibiting a yield strength in excess of 110 t.s.i. (245,000 p.s.i.: 175 kg./mm.^{2}) while maintaining a nil-ductility temperature below −60°C. (−75°F.). Its excellent notch tensile strength is another outstanding characteristic, and preliminary experiments have indicated the steel to be remarkably resistant to delayed cracking during exposure, in a highly stressed condition, in the corrosive environments so far tested. Ultra-high strength, combined with good ductility and toughness, is achieved by application of an extremely simple heat-treatment which does not involve quenching.

Information on the heat-treatment, mechanical properties, physical properties and fabrication of the steel is given below.

NOMINAL COMPOSITION

Carbon	0·03% max.
Silicon	0·1% max.
Manganese ..	0·1% max.
Nickel	17–19%
Cobalt	7–8%
Molybdenum ..	4·6–5·1%
Titanium	0·3–0·5%

The steel also contains small amounts of boron and zirconium.

HEAT-TREATMENT AND MECHANICAL PROPERTIES

Properties in the Annealed Condition

A suitable control of finish-rolling temperature, or heat-treatment at about 820°C. (1500°F.), followed by air cooling, develops an essentially carbon-free structure of the martensitic type. The steel has good machining characteristics In the annealed condition, the following typical properties are obtained:

0·2% proof stress	40–50 t.s.i. (90,000–100,000 p.s.i.: 63–70 kg./mm.^{2})
Ultimate tensile strength	60–65 t.s.i. (135,000–145,000 p.s.i.: 95–102 kg./mm)^2
Elongation	15–20%
Reduction-in-area	70–80%
Hardness	285-310 DPN (28-30 Rc)

Properties in the Hardened Condition

Hardening is effected by a simple treatment (designated 'mar-ageing') which results in precipitation hardening of the martensitic-type structure. This treatment involves heating for 3 hours at 450°-500°C. (840°-930°F.) followed by air cooling. Quenching is not required to develop optimum mechanical properties, even in large section sizes, and, consequently, the risk of distortion is much reduced.

Properties of Air-Melted Steels

The following properties have been achieved in air-melted material in the hardened condition:

0·2% proof stress	106–118 t.s.i. (235,000–265,000 p.s.i.: 165–185 kg./mm.^{2})
Ultimate tensile strength	112–124 t.s.i. (250,000–275,000 p.s.i.: 175–195 kg./mm.^{2})
Elongation	10–12%
Reduction-in-area	48–57%
Notch tensile strength* ..	165–172 t.s.i. (370,000–385,000 p.s.i.: 260–270 kg./mm.^{2})
Ratio of notch tensile strength to ultimate tensile strength ..	1·4–1·45

* 0·3 in. (7·5 mm.) diameter bar; theoretical notch-concentration factor = 10.

Charpy V-notch impact strength:	
At 20°C. (70°F.)	18–26 ft. lb. (2·5–3·6 kgm.)
At −73°C. (−100°F.) ..	14–16 ft. lb. (1·9–2·2 kgm.)
At −196°C. (−320°F.) ..	12–15 ft. lb. (1·6–2·1 kgm.)
Nil-ductility transition temperature (drop weight test)	less than −60°C. (−75°F.)
Endurance limit (10^8 cycles) ..	approx. 45 t.s.i. (100,000 p.s.i.: 70 kg./mm.^{2})

Attention is drawn to the outstanding properties of this steel relative to those of low-alloy steels of comparable strength. The ratio between notched- and plain-bar tensile strength of 1·4-1·45 is much superior to the values of 1-1·25 obtained from low-alloy steels with tensile strengths of the order of 120 t.s.i. (270,000 p.s.i.: 190 kg./mm.^{2}). Values for elongation and reduction-in-area are generally higher than, and the low-temperature properties are distinctly superior to, those of the latter steels.

Properties of Vacuum-Melted Steels

Although the steel is easily air-melted, toughness is much improved at highest strength levels by vacuum melting. In preliminary tests the vacuum-melted material has exhibited yield strengths of over 130 t.s.i. (290,000 p.s.i.: 205 kg./mm.^{2}) and notch tensile strengths of over 190 t.s.i. (425,000 p.s.i.: 300 kg./mm.^{2}), with Charpy V-notch impact energy of 22-25 ft. lb. (3·0-3·5 kgm.) at 20°C. (70°F.). The increased yield strength is obtained by modifying the above nominal composition as follows:

Cobalt	8–9%
Titanium	0·4–0·7%

FABRICATION

Hot and Cold Working

The 18 per cent. nickel-cobalt-molybdenum steel can be readily forged and hot rolled to a wide variety of shapes, and the low rate of work hardening during cold reduction permits extensive forming operations. The hardness of annealed material [285–310 DPN (28–30 R_C)] is increased to only 350 DPN (35 R_C) during 90 per cent. cold reduction.

Welding

Preliminary tests have shown that sound, crack-free welds can be produced in fully-heat-treated plate by use of coated-electrode or submerged-arc procedures. Yield strengths of over 100 t.s.i. (225,000 p.s.i.: 155 kg./mm.^{2}) have been obtained in 'mar-aged' welds of matching composition.

PHYSICAL PROPERTIES

Modulus of elasticity	$26·5–27·5 \times 10^6$ p.s.i.
Average coefficient of thermal expansion, 20°–500°C. (70°–900°F.) ..	10×10^{-6} per °C. ($5·6 \times 10^{-6}$ per °F.)
Density	8·0 gm. per c.c.

A patent application covering this new nickel steel has been filed.

ABSTRACTS OF CURRENT PUBLISHED INFORMATION ON NICKEL AND ITS ALLOYS

NICKEL

1st International Congress on Metallic Corrosion

See abstracts on pp. 130–37.

Determination of Trace Amounts of Cobalt in Nickel

V. T. ATHAVALE, S. V. GULAVANE and M. M. TILLU: 'Separation of Microgram Amounts of Cobalt in Nickel Metal by Tributyl Phosphate.'

Analytica Chimica Acta, 1960, vol. 23, Nov., pp. 487–90.

It is often necessary (particularly in the case of nickel used in the production of radio-cobalt) to determine microgram amounts of cobalt. Preliminary experiments demonstrated that tributyl phosphate extracts cobalt selectively at high hydrochloric-acid concentrations, and that the small amount of residual nickel does not interfere seriously in the subsequent determination with nitroso-R salt. In this paper the authors describe a method, evolved on this basis, which, it is stated, is applicable to the determination of cobalt in amounts as small as 5μg.

Purpose, Theory and Application of Nickel Dip in the Enamelling Industry

See abstract on p. 119.

A Nickel Complex Analogous to Cobalt Carbonyl

J. F. TILNEY-BASSETT: 'Cyclopentadienylnickel-Acetylene Complexes.'

Jnl. Chemical Soc., 1961, Feb., pp. 577–81.

It has been previously suggested that dicyclopentadienyl dinickel dicarbonyl is structurally similar to dicobalt octacarbonyl. In the study of the reactivity of this system with acetylenic compounds now reported, the author has obtained an acetylenic complex similar to that obtained with dicobalt octarcarbonyl.

It was found that dicyclopentadienyl dinickel dicarbonyl reacted with compounds containing two acetylenic bonds, yielding two different types of complex. Since there was good reason to conclude that one type of complex arose from reaction of one molecule of the dicyclopentadienyl compound with one of the acetylenic bonds, whereas, in the case of the other complex, a molecule of the dicyclopentadienyl compound reacted with each of the two triple bonds, the author took a sample of the former type of complex in an attempt to carry out a further reaction on the unreacted second triple bond. Success was not achieved in simpler types of reaction (such as hydrogenation), but it was found that the complex could be induced to react with iron and cobalt carbonyls to give complex molecules containing atoms of both nickel and iron or nickel and cobalt. Carbonyl-type derivatives containing two different transition metals were thus synthesized.

ELECTRODEPOSITION AND OTHER COATING METHODS

Corrosion of Decorative Nickel/Chromium Coatings

G. N. FLINT and S. H. MELBOURNE: 'The Corrosion of Decorative Nickel+Chromium Coatings: A Metallographic and Potential Study.'

Trans. Inst. Metal Finishing, 1961, vol. 38, Part 2, pp. 35–44.

In recent years, extensive studies have been made of nickel and chromium coatings in an attempt to improve their corrosion-resistance, and, as a result of this work, new types of coating have emerged (e.g., duplex nickel). The development of these improved coatings has depended to a large extent on the use of accelerated-corrosion tests. In the introductory section of the paper the authors suggest that all the accelerated tests in common use have been evolved on an empirical basis, the general principle followed being that of accelerating the rate of attack by increasing the concentration of those constituents whose presence in the natural environment is considered to be responsible for the corrosion encountered in service. Little attention appears to have been paid to the electrochemistry of such corrosion systems. When an accelerated test is used to evaluate different coating systems, however, a prime requirement is the ability to reproduce the form of corrosion which occurs in service, and the desirability of focusing attention on reproducing the form of attack, rather than on achieving breakdown at an accelerated rate, has been emphasized by LaQue (*Proc. Amer. Electroplaters' Soc.*, 1959, vol. 46, p. 141–8). In practice, more consideration

has been given to methods of reproducing the surface pattern of corrosion than to the morphology of the corrosion pits. The authors were prompted, in the light of these factors, to compare the occurrence and nature of corrosion experienced in service and in accelerated-corrosion tests. The initial results of this investigation, concerned with metallography and some electrochemical measurements of a preliminary nature, are described in the present paper.

The work was carried out in three phases:

(1) Typical specimens of nickel+chromium-plated car components, which had been in service for a number of years, were subjected to metallographic examination. The components were chosen to provide a variety of types of coating (incorporating bright, semi-bright and duplex nickel) deposited on steel and zinc substrates, and the periods of service to which the parts had been subjected varied widely. Nearly all the components had been exposed to a suburban/industrial-city environment.

(2) Examination of nickel+chromium-plated test panels after exposure to static-roof-corrosion and accelerated-corrosion tests. Four types of coating were tested, each having a nominal total thickness of 0·0015 in. (0·0375 mm.): details are given in the table below.

Thickness, in. × 10^{-3}			
Copper	Semi-Bright Nickel	Bright Nickel	Chromium
—	—	1·5	0·01
—	0·5	1·0	0·01
—	1·5	—	0·01
0·5	—	1·0	0·01

Plated panels were subjected to four accelerated-corrosion tests: (1) neutral salt-spray test, (2) acetic-acid/salt-spray test, (3) sulphur-dioxide test, (4) 'Corrodkote' test. Triplicate specimens were exposed on a roof in Birmingham.

(3) To obtain a better appreciation of the electrochemistry of the pitting corrosion observed, measurements were made of the anode polarization characteristics (in electrolytes simulating those used in the accelerated-corrosion tests) of wrought-steel specimens and electrodeposited foils of copper and dull, semi-bright and bright nickel.

The corrosion data presented are supplemented by photomicrographs typifying the pitting observed. The results obtained are deemed to warrant the following conclusions:

'1. Pit shapes characteristic of the early stages of service corrosion of semi-bright or bright-nickel+chromium coatings in industrial atmospheres are reasonably well reproduced by exposure to the acetic-acid/salt-spray, 'Corrodkote' and SO_2 accelerated-corrosion tests. The more irregular shape of pit frequently observed in nickel+chromium plating which has been in service for some years is not well reproduced by these accelerated tests.

'2. In copper+nickel+chromium coatings, none of the accelerated tests examined gives a faithful reproduction of the pitting corrosion experienced in service: contrary to service behaviour, the accelerated tests often corrode nickel in preference to copper. This feature is most marked in the SO_2 test, the results of which are therefore likely to give a misleadingly favourable impression of any protection provided by copper undercoats.

'3. In double-layer-nickel+chromium coatings, the acetic-acid/salt-spray and 'Corrodkote' tests reproduce fairly closely the flat-based pits, characteristic of service corrosion, which result from preferential corrosion of the bright-nickel layer. Exposure of this type of coating to the SO_2 test results in formation of the hemispherically-shaped pits characteristic of single-layer nickel coatings. The SO_2 test is insensitive to the different activities of the two types of nickel, and is not suitable for testing double-layer nickel coatings.

'4. Deductions made, on the basis of anode polarization measurements, regarding the direction of preferential corrosion are in accord with the results of metallographic observations.

'5. Further studies of anode and cathode polarization characteristics would provide a useful guide to the development of new tests capable of closely reproducing the form of corrosion observed in service.'

1st International Congress on Metallic Corrosion

See abstracts on p. 135.

Electrodeposition of Nickel-Copper Alloys from the Pyrophosphate Solution

S. K. PANIKKAR and T. L. R. CHAR: 'Electrodeposition of Nickel-Copper Alloys from the Pyrophosphate Bath.'

Jnl. Scientific and Industrial Research (India), 1960, vol. 19A, Oct., pp. 510–17.

Continuing their studies of the electrodeposition of metals and alloys from pyrophosphate solutions*, the authors have now established conditions for electrodeposition of nickel-copper alloys. In this paper they report studies of the influence of plating variables on alloy composition, cathode efficiency and cathode potential, and record the optimum conditions established for deposition of alloys containing 18–55 per cent. nickel. These conditions are reproduced on p. 118.

* See, in this connexion, papers on electrodeposition of nickel-zinc and nickel-cobalt alloys referred to in Nickel Bulletin, 1961, vol. 34, Nos. 2 and 3, and other abstracts in previous volumes of the Bulletin covering relevant work by the authors.

Solution composition

Nickel	0·3 *M* (17·6 g./L.)
Copper	0·05 *M* (3·2 g./L.)
Pyrophosphate-metal ratio	7†
pH	8·7
Temperature	60°C.
Specific resistivity	5·56 ohm/cm.[3]
Solution voltage	0·8–2·0 v.
Cathode	Platinum or copper
Anode-nickel, %	45·5
Cathode c.d.	0·25–5·00 amp./dm.[2]
Anode c.d.	0·06–1·25 amp./dm.[2]
Cathode efficiency	93–42 per cent.
Anode efficiency	Close to 100 per cent.
Cathode potential	0·73–1·17 v.
Throwing power (Gardam) (c.d. 0·5–4·0 amp./dm.[2])	57–14 per cent.

† P_2O_7 = 145·4 g./L.

Deposit

Composition, nickel	18–55 per cent.
Hardness	250–300 Vickers
Deposition time for 0·0005 in. (c.d. 1 amp./dm.[2])	68 min.

Efficiency and potential measurements demonstrated that cast alloy anodes are suitable for use with pyrophosphate solutions, and X-ray studies indicated that the alloy deposits have the same structure (f.c.c.) as nickel or copper coatings deposited from this type of solution.

See also

Electrodeposition of Nickel-Tungsten Alloys from the Pyrophosphate Solution

K. I. VASU and T. L. R. CHAR: 'Electrodeposition of Nickel-Tungsten Alloys from the Pyrophosphate Bath.'

Jnl. Scientific and Industrial Research (India), 1960, vol. 19B, Oct., pp. 413–4.

In this note the authors present the results of preliminary studies which have revealed the feasibility of co-depositing nickel and tungsten from the pyrophosphate solution.

The plating solution employed contained nickel pyrophosphate, sodium tungstate, ammonium citrate and potassium pyrophosphate. Addition of ammonium citrate prevented the occurrence of a black coating (which was otherwise found to form on the anode) and increased the cathode efficiency, the tungsten content of the deposit and the limiting current density.

Using platinum electrodes, satisfactory deposits (bright white in appearance, and ranging in nickel content from 47–94 per cent.) were deposited under the following conditions:

Solution composition

Nickel	0·025–0·38 *M*
Tungsten	0·005–0·7 *M*
Pyrophosphate	0·0625–0·95 *M* (molar ratio of pyrophosphate to nickel, 2·5)
Ammonium citrate	0·05 *M*
pH	7·7–10·3
Temperature	30°–90°C.
Solution voltage	1·9–5 v.
Cathode current density	30 amp./dm.[2] max.

Cathode efficiency varied from 5–74 per cent.

Data are tabulated to indicate the influence of the significant variables on deposit composition, cathode efficiency and potential. Of the addition agents studied, *p*-hydroxy azobenzene and gelatine were found to improve the brightness of the deposit. Ternary alloys containing copper, zinc, tin, iron or cobalt were obtainable by adding to the plating solution the respective metal pyrophosphates dissolved in potassium pyrophosphate.

Purpose, Theory and Application of Nickel Dip in the Enamelling Industry

N. S. C. MILLAR: 'The Purpose, Theory and Application of Nickel Dip.'

Metal Finishing Jnl., 1961, vol. 7, Feb., pp. 49–55.

In conventional two-coat enamelling (involving application of a soft groundcoat followed by a covercoat), a nickel dip or nickel flash is employed to permit greater latitude or tolerance in the general enamelling process. The advantages of nickel dipping are mentioned in the introduction of the present paper. It is pointed out in this connexion that nickel dipping improves the adhesion of the groundcoat (permitting it to be fired at lower temperatures, e.g., at the same temperature as the covercoat) and is reputed to minimize any fishscaling tendencies associated with the use of inferior steels. It has also been shown that nickel-dipped sheets do not copperhead. In the case of fully-acid-resistant blacks or A.R. self-mottle enamels applied directly to the steel, use of nickel dipping is imperative if the desired adhesion is consistently to be achieved. Several investigators are attempting, with varying degrees of success, to apply covercoat super-opaque enamels direct to steel, and in this application nickel dipping is again considered essential. Use of the technique is also deemed a prerequisite for achievement of consistently high adhesion in enamelling with low-firing groundcoats and covercoats. Radiation Enamels, Ltd., the company with which the author is associated, has had 12 years' experience in the application of nickel dipping. The present review, based on this experience, covers the theoretical factors involved in nickel dipping, the practical application of the process, and the advantages it offers in relation to the various types of enamel with which it has been used.

Following discussion of the factors contributing to the beneficial effects of nickel dipping, and consideration of the principles underlying the deposition of a nickel flash by the two methods employed in enamelling (the galvanic and the chemical-reduction process), the author comments upon practical experience, and the variables involved, in the application of a galvanic nickel dip incorporated in a pickling cycle with which he has had considerable experience. Attempts to increase the amounts of nickel deposited, and the success achieved, are alluded to.

Nickel dipping by the reduction method is briefly surveyed, reference is made to the availability of

the nickel-coated sheet steel 'Nitec', and the procedure employed in de-enamelling nickel-dipped sheets is outlined. In subsequent sections the author draws attention to the advantages associated with, and the procedures involved in, enamelling nickel-dipped sheet with a soft groundcoat, A.R. self mottles, A.R. black groundcoats and low-temperature enamels.

In the concluding section on pre-enamelling cycles employed in the direct application of a covercoat on steel, emphasis is placed on the important rôle played by nickel dipping. The overall conclusion is that 'all future developments in the sheet-iron vitreous-enamelling industry are dependent upon nickel dip, and the author cannot overstress the advantages arising from this process'.

In an appendix to the paper a résumé is given of the analytical procedures employed in determining nickel (1) in the nickel-dip solution (using disodium ethylenediamine tetra-acetate and murexide indicator), (2) in the nickel-dip solution (using potassium cyanide), (3) on steel plates (using the dimethylglyoxime method).

NON-FERROUS ALLOYS

Chromium and Nickel Solvuses in the Chromium-Nickel System

C. J. BECHTOLDT and H. C. VACHER: 'Redetermination of the Chromium and Nickel Solvuses in the hromium-Nickel System.'

Trans. Metallurgical Soc., A.I.M.E., 1961, vol. 221, Feb., pp. 14-18.

A recent compendium* of the constitution of binary alloys gives two diagrams for the chromium-nickel system, one indicating a simple eutectic, the other showing a eutectoid and a eutectic. The eutectoid (approximate temperature 1200°C.; approximate composition 30 at. per cent. nickel) was the result of an allotropic transformation in a high-temperature solid-solution form of a chromium-rich phase, β. In a preliminary study, carried out by the National Bureau of Standards within the scope of work on the solid-state reactions occurring in high-temperature alloys containing iron, chromium, molybdenum and nickel, there was no indication of transformation in the chromium-rich phase of ternary and quaternary alloys in which chromium and nickel were the major components. A systematic study was therefore made of the constitution of a range of heat-treated chromium-nickel alloys. The compositions of the alloys were selected so as to permit determination of the boundaries of the chromium-rich and nickel-rich phases, and exploration, at small intervals, of the ranges of composition and temperature in which the eutectoid had been reported. The results of this study are recorded and discussed in the present paper.

The alloys, varying in nickel content from 5-95 wt. per cent., and produced by powder-metallurgical methods, were heated in dry hydrogen to the desired temperature (800°-1450°C.), and then examined by microscopical and X-ray-diffraction methods.

The results are incorporated in a revised chromium-nickel phase diagram. The diagram differs slightly from the simple eutectic diagram given by HANSEN, in that the determination of the chromium solidus has been extended from 1345°C. to 1450°C., and the maximum solubility of nickel in chromium has been found to be 38, instead of 32, at. per cent. nickel. The examination of alloys differing slightly in composition and heat-treatment revealed no evidence of a β phase or eutectoid formation in the microstructure.

* M HANSEN: 'Constitution of Binary Alloys', *Metallurgy and Metallurgical Engineering Series, McGraw-Hill Book Company, 2nd Edition, 1958.*

1st International Congress on Metallic Corrosion

See abstracts on pp. 130-37.

Influence of Metal/Mould Reaction and Section Thickness on the Properties of Nickel-containing Gunmetal Castings

F. HUDSON: 'Effect of Metal-Mould Reaction and Section Thickness on the Properties of Gunmetal Castings.'*

Brit. Foundryman, 1961, vol. 65, Mar., pp. 137-46.

In a previous paper (see abstract in *Nickel Bulletin*, 1958, vol. 31, No. 12, pp. 320-1) the author and his co-workers showed that, in the case of alloys with a wide freezing range, such as tin-bronze and gunmetal, the properties of castings could vary widely with section thickness, and were unrelated to those obtained from separately-cast test bars. Furthermore, it was evident that composition had an important bearing on the section sensitivity of gunmetal alloys. In the case of 85-5-5-5 leaded-gunmetal castings, the mechanical properties in thick sections were seriously reduced through the presence of massive grain-boundary lead segregates, in addition to a variable amount of micro-porosity. The addition of 2 per cent. nickel, however, promoted finer dispersion of the lead particles and a much more uniform and higher level of properties in leaded-gunmetal castings of varying section. From a study of the data given, it was apparent that none of the standard gunmetals then available was capable of providing the ideal combination of properties needed for the production of quality castings, namely a uniformly high level of mechanical properties and pressure-tightness in castings of variable section. It was concluded that an alloy containing 6-7 per cent. tin, 3-4 per cent. zinc, 3-4 per cent. lead, 1½-2½ per cent. nickel, balance copper, might provide this ideal. Furthermore it was thought that the mechanical

* *We shall be pleased to supply a free reprint of this paper.*

properties of castings in such an alloy could probably be related to those obtained from separately-cast test bars. Subsequent work by PATTON confirmed these conclusions (*ibid.*, 1960, vol. 53, Feb., pp. 82–7; abstract in *Nickel Bulletin*, 1960, vol. 33, No. 4, pp. 79–80).

In both of the investigations referred to above, the effects of section thickness were assessed from mechanical properties obtained on relatively small test bars machined from the centre of experimental step-bar and wedge castings. Design data determined in this way, especially for sections over 1 in. (2·5 cm.) in thickness, are obviously indicative of the minimum properties likely to be obtained, and are not representative of the properties throughout a particular casting section. Moreover, the incidence of a variable degree of dispersed micro-porosity, probably due to metal/mould reaction, and particularly troublesome at the centre of 4-in. (10-cm.) thick sections, may have had an effect on the results obtained. The investigation reported in the present paper was undertaken to explore these factors.

Large tensile test bars, 3 ft. (0·9 m.) long, 4 in. (10 cm.) in diameter in the breaking area, and weighing about 300 lb. (136 kg.), were made in 90–10 zinc-free bronze, 88–10–2 gunmetal, and in 87½–7½–2–3, 85–6½–3–3½–2Ni and 85–5–5–5 leaded-gunmetals. Standard tensile-test bars were cast at the same time.

Three series of large tensile-test bars were cast in each of the alloys studied. The residual phosphorus and mould moisture contents were varied to obtain (*a*) no metal/mould reaction, (*b*) a small amount of metal/mould reaction, and (*c*) a substantial amount of mould/metal reaction. After machining, the large tensile bars were broken on a 1,000-ton testing machine.

Cross-sectional discs were cut from the threaded grip portion of the broken bars for density determinations, metallurgical examination, and for the provision of corrosion- and erosion-test specimens.

The author's discussion of the test data presented leads him to conclude that:

'(1) The effect of metal/mould reaction has an important bearing upon the sensitivity of gunmetal and tin-bronze to variation in casting section.

'(2) A small amount of metal/mould reaction, such as can arise by casting a 4-in.-diameter gunmetal bar containing 0·02–0·04 per cent. phosphorus into a dry-sand mould baked for 24 hours at 400°C. (725°F.), is sufficient to promote micro-porosity and reduce mechanical properties below specification requirements.

'(3) At higher phosphorus and mould-moisture levels, the degree of metal/mould reaction in thick-sectioned gunmetal castings becomes pronounced, leading to the presence of gross porosity, in addition to micro-porosity, and a decrease of 30–40 per cent. in ultimate tensile strength with a 50–75 per cent. reduetion in ductility.

'(4) When metal/mould reaction is suppressed, the mechanical properties of thick-sectioned gunmetal castings, containing more than 7 per cent. tin and less than 3 per cent. lead, are nearly equivalent to those obtained from separately-cast test bars.

'(5) In leaded gunmetals containing less than 7 per cent. tin and more than 3 per cent. lead, which are acknowledged as being most suitable for the production of castings which have to withstand pressure, the properties of thick-sectioned castings are well below those obtained from separately-cast test bars, even when metal/mould reaction is suppressed.

'(6) The fall in properties in thick-sectioned leaded-gunmetal castings, caused by the weakening effect of massive grain-boundary lead segregates, can be overcome by the addition of 2 per cent. nickel, enabling maximum strength and pressure-tightness to be obtained.

'(7) A gunmetal containing 6–7 per cent. tin, 3–5 per cent. zinc, 3–5 per cent. lead, 1½–2½ per cent. nickel, balance copper, is capable of producing thick-sectioned castings having the mechanical properties of 88–10–2 combined with the degree of pressure-tightness normally associated with 85–5–5–5 gunmetal.'

Nickel-containing Spring Alloys for Special Applications

See abstract on p. 128.

Use of Cupro-Nickel for Fin Drums Drying Calcium-Carbonate Paste

L. W. GLEEKMAN and R. K. SWANDBY: 'Massive De-Aluminization of Aluminium Bronze by Chloride Crevice Attack.'

Corrosion, 1961, vol. 17, Mar., pp. 144t–8t.

The paper comprises a case history of the failure of a wrought aluminium-bronze fin drum (aluminium 6–8, iron 1·5–3·5, per cent.) employed in the drying of a calcium-carbonate paste.

Selective attack, established as due to de-aluminization, occurred not only along the 7 ft. 6 in. longitudinal weld (where two phases were present), but also along the entire periphery of the 250 fins machined into the outer face of the drum (which were all single-phase). The calcium-carbonate paste was essentially neutral (pH 8), containing only 0·2 per cent. NaCl and Na_2SO_4 as minor impurities. The interior of the drum was exposed to saturated steam at 350°F. (180°C.). Associated with the failure was a hardened deposit of $CaCO_3$ and $CaSO_4$, which acted as a crevice around the fins and in the grooves. Laboratory tests revealed that de-aluminization occurred only when chloride was present in a crevice. No attack resulted in the presence of chemically pure $CaCO_3$ and distilled water or $CaSO_4$ and water.

A solution to the problem was found in the use of 90–10 cupro-nickel. Drums constructed from this alloy (using 70–30 cupro-nickel as the welding material) are stated to have been in operation for two years with no signs of corrosive attack. Although the coefficient of heat transfer of the cupro-nickel

is somewhat lower than that of aluminium-bronze, it is concluded that the higher corrosion-resistance and strength of the cupro-nickel render it an ideal material of construction for this type of service.

CAST IRON

Resistance of Cast Irons to Thermal Fatigue

See abstract on p. 126.

Use of 'Ni-Hard' in Crushing and Grinding Plant

O. NICKEL: ''Ni-Hard': A Wear-Resistant Material for Crushing and Grinding.'

Aufbereitungs-Technik, 1960, vol. 1, No. 9, pp. 371–84.

'Ni-Hard', a martensitic white iron (containing in the region of 4 per cent. nickel and 2 per cent. chromium, and characterized by extremely high hardness and abrasion-resistance), has, since its development some decades ago, found wide application as a wear-resistant material. In such industries as the mining and cement, the materials of construction used in crushing and grinding plant are subjected to severe abrasion, and the cost involved in their replacement is considerable. This article was written with the aim of outlining the properties of 'Ni-Hard' and drawing attention to the technical and economic advantages which the iron offers as a material of construction for grinding plant.

Following discussion of production procedures, the author comments upon data tabulated on mechanical and physical properties, and then discusses the heat-treatments to which the iron is usually subjected. Methods of increasing impact properties (e.g., to satisfy the requirements of applications involving exposure to both abrasion and impact) are considered, and machinability and welding characteristics are also taken into account. Data are presented in illustration of the extremely high wear-resistance exhibited by 'Ni-Hard'.

The main section of the review is concerned with the applications for which 'Ni-Hard' has been found suitable in (1) the cement industry, (2) mining and ore preparation, (3) Renn plant, (4) coke and coal crushing, (5) pumps, and (6) the stone and earth industry. Case histories indicate the performance of 'Ni-Hard' in the six fields covered, and components typical of those for which the iron is used are illustrated.

CONSTRUCTIONAL STEELS

Morphology of Martensite in Nickel-containing Steels

See abstract on p. 130.

Structure of Bainite in Hypoeutectoid Steels

S. J. MATAS and R. F. HEHEMANN: 'The Structure of Bainite in Hypoeutectoid Steels.'

Trans. Metallurgical Soc., A.I.M.E., 1961, vol. 221, Feb., pp. 179–85.

The authors present, and discuss, the results of research in which a study was made of the influence of heat-treatment and composition on the structure of bainite in chromium-nickel, nickel-chromium-molybdenum, chromium-molybdenum-vanadium and chromium hypoeutectoid steels.

The results are regarded as confirming the existence of two distinct forms of bainite (upper and lower) in hypoeutectoid steels. The transition between the two forms occurs at about 650°F. (345°C.), irrespective of the alloy content of the steel, and their structural differences can, it is considered, be interpreted in terms of the kinetics of carbide precipitation from supersaturated ferrite.

Properties of Nickel-Aluminium Age-Hardening Nitriding Steel

J. B. SEABROOK: 'Properties of Ni-Al Age-Hardening Steel.'

Metal Progress, 1961, vol. 79, Feb., pp. 80–3.

The investigation described originated in studies of the ageing characteristics of nickel-aluminium nitriding steels, in which it was found that: (*a*) almost regardless of prior history (for example, normalizing, quenching and tempering up to 1100°F. (595°C.), quenching only, quenching to and holding at the ageing temperature), such steels age to a final hardness range characteristic of the ageing temperature; (*b*) the steels do not over-age even though held at temperature for 100 hr. or more (although a quenched specimen may go through a peak of higher hardness before levelling off at the characteristic hardness); (*c*) a specimen aged at one temperature, and then aged at a higher or lower temperature, will approach the hardness characteristic of the second temperature; and (*d*) slow rates of cooling from the solution temperature result in some initial hardening, but do not prevent subsequent ageing to essentially full hardness. In view of these findings, the introduction by The International Nickel Company, Inc., of a 5%Ni-2%Al age-hardenable nitriding steel (*see* abstract in *Nickel Bulletin*, 1960, vol. 33, No. 6, pp. 143–4) prompted the authors to carry out the study of its mechanical properties now reported.

In the initial phase of the study, considerable work was conducted to evaluate normalizing, quenching and tempering, and ageing treatments. Before ageing, the steel* is usually normalized at 1700°F. (925°C.), austenitized at 1650°F. (900°C.), oil-quenched to Rockwell C44–46, and tempered at 1275°F. (690°C.) to Rockwell C35–38. Ageing at 975°F. (520°C.) yielded a hardness of Rockwell C46–49, while ageing at 1050°F. (565°C.) resulted in a hardness of Rockwell

* Carbon 0·23, manganese 0·42, silicon 0·25, phosphorus 0·013, sulphur 0·023, nickel 5·3, aluminium 2·3, chromium 0·55, molybdenum 0·24, vanadium 0·14, per cent.

Stress-Rupture Properties of Nickel-Aluminium Nitriding Steel

(See abstract on p. 122)

Test Temperature		Initial Stress			Time-to-Fracture, hours	Elongation in 1 in.	Reduction-in-Area
°F.	°C.	p.s.i.	t.s.i.	kg./mm.²		%	%
			TREATMENT A				
900	480	80,000	35·5	56·5	577	18	40
900	480	85,000	38·0	60	165	25	70
900	480	90,000	40·0	63·5	30	25	70
900	480	90,000	40·0	63·5	44	30	70
1000	540	65,000	29·0	45·5	31	17	45
1000	540	70,000	31·0	49·0	81	17	30
1000	540	75,000	33·5	53·0	17	27	80
			TREATMENT B				
900	480	70,000	31·0	49·0	529	Did not break	
900	480	80,000	35·5	56·5	387	18	60
900	480	90,000	40·0	63·5	0·5	24	70
1000	540	60,000	27·0	42·0	120	16	20
1000	540	60,000	27·0	42·0	210	14	15
1000	540	70,000	31·0	49·0	8	27	50

C37–40. It was also found that tempering at 800°F. (425°C.), followed by ageing at 975°F. (520°C.), produced a hardness of Rockwell C51–54.

In subsequent tests the properties of the steel were therefore studied as a function of three heat-treatments. All specimens were heat-treated as previously described up to the quench, then one set was tempered at 1275°F. (690°C.) and aged at 975°F. (520°C.) (Treatment A); the second set was merely tempered at 1275°F. (690°C.) (Treatment B); and the third set was tempered at 800°F. (425°C.) and aged at 975°F. (Treatment C).

Tensile, fatigue, Charpy V-notch impact, and stress-rupture tests were conducted, and thermal-expansion and dimensional changes during ageing were determined for specimens subjected to Treatment A. Distortion during ageing was studied on specimens submitted to Treatments A and C. A tentative evaluation was made of the effects of varying the ageing treatment.

Forging was found to present no problems, and machinability was good despite the fairly high intermediate hardnesses at which the specimens were finish-machined.

Curves for the several ageing temperatures studied illustrate the lack of over-ageing and the 'levelling-off' feature previously mentioned.

The results of the tensile tests show the steel to exhibit good yield to tensile ratios, and, except for ductility (13 per cent., 17 per cent. and nil elongation with Treatments A, B and C, respectively), the values agree with those which would be expected from a conventional quenched-and-tempered steel.

With regard to the fatigue data, Treatments A and B yielded results similar to those for conventional steels, but Treatment C resulted in an endurance-limit/tensile-strength ratio of 0·31 (presumably due to brittleness). The fatigue strength of test pinions was about equal to that of through-hardened steel pinions at Rockwell C35.

Though impact strengths were relatively low, they could, it is considered, be markedly increased, with little loss of hardness, by appropriate heat-treatment.

The distortion tests indicate that distortion during ageing is sufficiently low to permit finish-machining before ageing.

Stress-rupture results for conditions A and B are reproduced in the table above.

On the basis of the data presented (derived from one heat of steel), the material is considered to offer the advantages of moderate material cost, low processing cost, good forgeability and machinability, low distortion, strengths similar to conventional steels, and aged hardnesses up to Rockwell C53.

Resistance of Nickel-containing Steels to Thermal Fatigue

See abstract on p. 126.

1st International Congress on Metallic Corrosion

See abstracts on pp. 130–37.

HEAT- AND CORROSION-RESISTING MATERIALS

Investment Castings in High-Alloy Steels and Nickel- and Cobalt-base Alloys: British Standard

BRIT. STANDARDS INSTN.: 'Specification for Investment Castings in Metal: Part 2. High Alloy Steels, Nickel and Cobalt Alloys.'

B.S. 3146: *Part* 2: 1961; 33 pp. Price 8/6.

The Standard* lays down requirements for investment castings in high-alloy steels and nickel- and cobalt-base alloys suitable for applications requiring corrosion-, heat-, and wear-resistance.

Section One specifies general requirements relating to the manufacturing process, composition, fettling and dressing, heat-treatment, methods of testing, etc. Section Two stipulates the composition limits, condition of delivery, heat-treatment, mechanical properties, and tests specific to each of the grades of material covered. The designations of the grades are noted below.

Type ANC 1: 13 per cent. Chromium Steel Castings (for general engineering purposes where resistance to corrosion is required).

Type ANC 2: 18 per cent. Chromium Steel Castings (for use where resistance to corrosion is required).

Type ANC 3: Austenitic Chromium-Nickel Steel Castings (for use where resistance to corrosion is required).

Type ANC 4: Austenitic Chromium-Nickel-Molybdenum Steel Castings (for general engineering purposes where resistance to corrosion is required).

Type ANC 5: Nickel-Chromium Steel Castings (having resistance to scaling at elevated temperatures).

Type ANC 6: Chromium-Nickel Steel Castings (which combine good corrosion- and heat-resisting properties).

Type ANC 7: Chromium-Nickel-Cobalt Steel Castings (suitable for stressed components operating at elevated temperatures).

Type ANC 8: Nickel-Chromium Castings (having high oxidation-resistance and good welding properties).

Type ANC 9: Nickel-Chromium-Titanium Castings (having good resistance to creep at temperatures up to at least 750°C.).

Type ANC 10: Nickel-Chromium-Cobalt-Titanium Castings (having good resistance to creep up to at least 870°C.).

Type ANC 11: Nickel-Chromium-Cobalt-Molybdenum Castings (having good resistance to thermal shock up to 1100°C.).

Type ANC 12: Nickel-Chromium-Molybdenum-Titanium Castings (having good resistance to thermal shock).

Type ANC 13: Cobalt-Chromium-Nickel-Tungsten Castings (having high resistance to creep and thermal shock).

Type ANC 14: Cobalt - Chromium - Molybdenum Castings (having a high resistance to wear and thermal shock).

Type ANC 15: Nickel-Molybdenum Castings (having high resistance to corrosion by hot concentrated hydrochloric acid).

Type ANC 16: Nickel - Molybdenum - Chromium Castings (for applications where resistance to corrosion by oxidizing acids is required).

Type ANC 17: Nickel-Silicon Castings (for applications where resistance to corrosion by sulphuric acid is required).

Type ANC 18: Nickel-Copper-Silicon Castings (for applications where resistance to mineral-acid and salt-water corrosion is required).

* *Part* 1 covering carbon steels and low-alloy steels was referred to in *Nickel Bulletin*, 1959, vol. 32, No. 12, p. 359.

Chromium and Nickel Solvuses in the Chromium-Nickel System

See abstract on p. 120.

Intragranular Precipitation of Intermetallic Compounds in Nickel-containing Austenitic Alloys

H. J. BEATTIE and W. C. HAGEL: 'Intragranular Precipitation of Intermetallic Compounds in Complex Austenitic Alloys.'

Trans. Metallurgical Soc., A.I.M.E., 1961, vol. 221, Feb., pp. 28-35.

In a previous paper the authors reported an investigation of the secondary-phase reactions occurring, during solution- and ageing-treatment, in alloys hardenable by precipitation of γ', and commented upon data relating to cellular precipitation and its interaction with general precipitation (see abstract in *Nickel Bulletin*, 1960, vol. 33, No. 3, p. 51). The group of alloys selected for study in the work now described exhibit precipitation-hardening reactions involving two distinct classes of intermetallic compound, the predominating class appearing to depend on base composition. Their compositions are given in the table on p. 125.

Specimens were solution-treated in the range 1700°-2200°F. (925°-1205°C.), aged in the range 1200°-1800°F. (650°-980°C.) at logarithmic time intervals up to 1000 hours, and then examined by electron microscopy and X-ray-diffraction techniques.

The following conclusions are drawn from the data and photomicrographs included in the paper:

'(1) The principal phases which precipitate during the ageing of 'S-816' and 'S-590' are M_6C and Laves phase, while thermally inert CbC is always present. The higher cobalt content of 'S-816' increases the solutioning capacity for M_6C and Laves phase.

'(2) The high aluminium and titanium content of 'René 41' results in a high solutioning temperature for γ'. The γ'-precipitation predominates at early stages, and late precipitation of μ phase occurs in Widmanstätten form. $M_{23}C_6$ precipitates at grain boundaries and later transforms to M_6C, while TiC dissolves to generate more γ' and M_6C.

Composition of Alloys Subjected to Metallographic Study (wt.%)

(*See abstract on p. 124*)

Type	C	N	Al	Ti	Fe	Ni	Co	Cr	Mo	W	Si	Mn	Zr	Nb	Ta	P	S	B
'S-816'* ..	0·38	0·02	—	—	4·46	19·39	41·96	19·81	3·97	3·87	0·56	1·22	—	3·95	0·38	0·02	0·02	—
'S-590'* ..	0·41	0·07	—	—	23·75	19·91	20·97	20·36	4·20	4·43	0·63	1·29	—	4·02	—	0·02	0·01	—
'René 41'† ..	0·09	—	1·63	3·21	0·3	54·75	11·22	18·88	9·79	—	0·10	0·04	—	—	—	—	—	—
High-boron 'Incoloy 901'†	0·04	0·005	0·19	2·42	34·99	42·87	—	12·62	6·10	—	0·21	0·49	—	—	—	—	0·007	0·1
Low-boron 'Incoloy 901'†	0·04	—	0·18	2·40	33·09	41·81	0·37	13·11	6·12	—	0·54	1·50	—	—	—	—	0·007	0·001
'M-308'† ..	0·05	0·01	0·33	1·80	42·43	32·80	—	13·10	3·30	6·00	—	—	0·18	—	—	—	—	—
'M-647'† ..	0·04	0·01	0·56	2·70	51·32	23·80	—	15·80	5·60	—	—	—	0·17	—	—	—	—	—

* Air-melted and forged into $\frac{3}{8}$-in. (2·1-cm.) bar stock. † Vacuum-melted and forged into $\frac{3}{8}$-in. (1·5-cm.) bar stock.

'(3) High-boron 'Incoloy 901' contains a refractory boride, M_3B_2; precipitation of γ', μ phase, and a characteristic etch-pitting occur on ageing. No etch-pitting is observed in low-boron 'Incoloy 901'; γ', Ni_3Ti and Laves phases form on ageing, the Ni_3Ti by transformation from γ'.

'(4) Both 'M-308' and 'M-647' are precipitation-hardened in the early stages of ageing by metastable γ', which redissolves when μ phase appears in 'M-308' and σ and χ phases appear in 'M-647'.

'(5) There is a correlation between matrix composition and the tendency to precipitate simple ordered close-packed structures on the one hand, and complicated intermetallic structures on the other. This effect is related to a crystal-chemistry phenomenon first reported by Laves and Wallbaum.'

Study of Carbides Present in 'Waspaloy'

J. F. RADAVICH and W. J. PENNINGTON: 'Carbides in 'Waspaloy'.'

Metal Progress, 1961, vol. 79, Feb., pp. 94–6.

In recent years much work has been carried out to identify the carbide phases present in nickel-base high-temperature alloys. These investigations indicate that Ti(C,N) is one of the primary phases which occur in such alloys (a minor amount of titanium nitride being also present). The other carbide phases M_6C and $M_{23}C_6$ may also occur, depending upon composition and heat-treatment: the former is often observed in alloys containing over 5 per cent. molybdenum, while the latter has been determined in most high-temperature alloys. The work now described was initiated to supplement previous research by a study of the carbides in 'Waspaloy',* selected as a typical 'superalloy'.

The experiments, carried out on three vacuum-induction-melted heats of 'Waspaloy', were designed to determine the effects of solution heat-treatment, and subsequent stabilizing and ageing heat-treatments, on the occurrence of the carbide phases. Representative samples from each heat were divided into two groups: the first was solution-treated for 4 hours at 1975°F. (1075°C.) and air-cooled to room temperature; the second group was solution-treated for 4 hours at 1975°F. (1075°C.), air-cooled, stabilized for 24 hours at 1550°F. (840°C.), air-cooled, and then aged for 16 hours at 1400°F. (760°C.). After electrolytic polishing and etching, replicas were taken from each sample and examined under the electron microscope. Residues were examined by X-ray diffraction and fluorescent techniques.

The authors' review of the data obtained (micrographs typifying the structures observed are included in the article) leads them to conclude that the primary carbide phase in vacuum-induction-melted 'Waspaloy' is an MC-type carbide which is high in titanium and molybdenum, but includes smaller amounts of nickel, chromium and zirconium. Subsequent ageing appears to break down the phase, and a secondary carbide precipitate ($M_{23}C_6$) forms which is predominantly chromium-rich but contains small amounts of nickel, molybdenum and cobalt. The $M_{23}C_6$ phase forms primarily at the grain boundaries, and precipitation of this phase within the matrix then ensues.

* Typical composition: nickel 56, chromium 19·5, cobalt 13·5, molybdenum 4, iron 1, titanium 3, aluminium 1·3, carbon 0·05, boron 0·005, zirconium 0·06, per cent.

Diffusion of Brazing-Alloy Constituents into Heat-Resisting Materials

W. FEDUSKA: 'The Nature of the Diffusion of Brazing-Alloy Elements into Heat-Resisting Alloys.'

Welding Jnl., 1961, vol. 40, Feb., pp. 81s–9s.

In a previous paper, the author reported the results of an investigation of the microstructural and microhardness characteristics of a variety of high-temperature brazing-alloy/basis-metal interfaces*. The investigation formed one stage of a series of fundamental studies in progress in the laboratories of

* *Ibid.*, 1958, vol. 37, Feb., pp. 62s-73s: abstract in *Nickel Bulletin*, 1958, vol. 31, No. 6, pp. 177-9. Details of a study of wetting reactions were given in a paper referred to in *Nickel Bulletin*, 1959, vol. 32, No. 6, pp. 201-2.

Composition of High-Temperature Alloys used in Diffusion Experiments

(*See abstract on p. 125*)

Material	C %	Mn %	Si %	Cr %	Ni %	Co %	Mo %	W %	Nb/Ta %	Ti %	Al %	Fe %
Type 410* martensitic stainless steel	0·15 max.	—	—	11·5-13·5	—	—	—	—	—	—	—	Bal.
Type 347* austenitic stainless steel	0·08 max.	—	—	17·0-19·0	9·0-13·0	—	—	—	0·8 min.	—	—	Bal.
Alloy 3†	0·03	0·8	0·8	13·5	26·0	—	3·0	—	—	1·6	0·1	Bal.
Alloy 4†	0·04	0·7	0·3	15·0	Bal.	—	—	—	0·9	2·5	0·9	7·0
Alloy 5†	0·10	1·5	0·7	20·0	10·0	Bal.	—	15·0	—	—	—	1·0

* Nominal composition. † Actual composition.

Westinghouse Electric Corporation, which, undertaken to throw light on the fundamental factors governing the formation of brazed joints, led to a qualitative understanding of the diffusion mechanisms encountered and the microstructures produced during high-temperature-alloy brazing. Since lack of analytical equipment or techniques prevented any quantitative determination of the nature of the grain-boundary constituents or solid-solution regions at the brazed-joint interfaces, work was subsequently carried out to establish the individual and combined effects of elements usually present in high-temperature brazing alloys.

In these experiments, which form the subject of the present paper, the individual effects of boron, carbon, chromium, iron, nickel and silicon were studied by placing plate specimens of five high-temperature materials (see table above) in contact with the particular element under examination (which, in powder form, was packed around the plate specimen), and heating under a protective atmosphere, at a predetermined temperature and for a predetermined time, to induce diffusion into the high-temperature material. Subsequently, similar diffusion tests were conducted with various binary-element powder combinations, including the following: boron-carbon, boron-chromium, boron-iron, boron-nickel, boron-silicon, carbon-chromium, carbon-iron, carbon-nickel, carbon-silicon, chromium-iron, chromium-nickel, chromium-silicon, iron-nickel, iron-silicon and nickel-silicon.

After cooling to room temperature, the plate specimens were removed from the furnace, cleaned of any loose powder, and sectioned transversely for microscopical examination. After examination for evidence of diffusion, microhardness measurements were made in the reaction zones. The data obtained were then compared with the interface reaction structures and microhardness results derived, in the previous study, from joints produced between commercial high-temperature brazing alloys and the same basis materials. The maximum visible depth of diffusion penetration was established, but determination of diffusion coefficients was not considered to be within the scope of the experiments.

Full details are given of the results of the research, and diffusion mechanisms are discussed. The conclusions drawn are quoted below.

'1. The interstitial carbon atom, the small boron atom, and sometimes the substitutional silicon atom, rapidly diffuse along grain boundaries at brazing temperatures of about 1740°-2190°F. (950°-1200°C.).

(*a*) These elements irrigate into adjoining grain regions.

(*b*) These elements also migrate by incipient volume diffusion into the base-metal surface grains.

(*c*) Wherever these elements diffuse, they can, and do, react with base-metal elements to form borides, carbides or silicides.

'2. Substitutional atoms—chromium, iron, nickel and, generally, silicon—slowly penetrate by volume diffusion into the various base metals.

'3. Atoms of the substitutional elements form solid solutions with base-metal atoms at the interface diffusion-reaction regions.

'4. In binary combination with other elements, each element diffuses according to its individual diffusion mechanism into a particular base metal.

'5. The isolated diffusion mechanisms observed for the various elements are in accordance with bonding reaction mechanisms derived from a comprehensive study of commercial-brazing-alloy reactions with the same high-temperature alloys.

'6. Sometimes, diffusing silicon reacts with nickel (in Alloy 3, Alloy 4 and Alloy 5) to form a nickel-silicon-rich eutectic at the sample surface region.'

Resistance of Nickel-containing Alloys and Steels to Thermal Fatigue

H. G. BARON and B. S. BLOOMFIELD: 'Resistance to Thermal-Stress Fatigue of some Steels, Heat-Resisting Alloys, and Cast Irons.'

Jnl. Iron and Steel Inst., 1961, vol. 197, Mar., pp. 223-32.

In the investigation reported, the thermal-fatigue tests were carried out using a technique in which one surface of the specimen was repeatedly heated while the main mass was continuously water-cooled. The

specimen was of truncated wedge form, the narrow edge being heated to give uniaxial thermal stresses in the direction of the edge. Thermal expansion in the direction of the edge was not completely restrained, some 20 or 30 per cent. of the total expansion being lost (largely in bending of the specimen). Heating was effected by h.f. induction, and the specimen was heated for between 1·0 and 1·3 seconds. The cooling time fell within the range 0·1–20 seconds. Temperatures were measured by fine-gauge thermocouple wires spot-welded to the surface and connected to a high-speed galvanometer, which was arranged so that part of the reflected beam operated photocells to give automatic control of the maximum and minimum temperatures in the cycle.

In the initial part of the paper the authors present, and discuss, data (mainly on En 25 2½ per cent. nickel-chromium-molybdenum steel) illustrating the influence, on thermal fatigue life, of the temperature cycle, phase changes, stress concentration and interaction of cracks. Fatigue-life curves are presented in illustration of the influence of the maximum and minimum temperatures in the cycle, and emphasis is placed on the important rôle played by martensite transformation if it occurs in every temperature cycle. In evaluating the effects of the peak temperature, the minimum temperature in each cycle was held constant at 40°C.

In the second section of the paper, the authors summarize the results of tests carried out to gain comparative data on the behaviour of various materials in thermal-stress fatigue, and, in particular, to evaluate the influence of the peak cyclic temperature on fatigue life.

Fatigue-life curves are recorded for the following materials:

Steels (cycled to peak temperatures in the range 400°–1050°C.): soft iron bar; 0·5 per cent. molybdenum steel bar; 1 per cent. chromium-molybdenum bar; 0·66 per cent. carbon ingot; 0·89 per cent. carbon bar; 3 per cent. nickel-chromium-molybdenum casting; 2 per cent. silicon-nickel bar; 3 per cent. chromium-molybdenum forging; 7 per cent. chromium-silicon forging; 2 per cent. silicon-molybdenum bar; 2·5 per cent. nickel-chromium-molybdenum bar; 1 per cent. silicon-copper-molybdenum-vanadium bar; 9 per cent. tungsten-chromium forging.

Cast Irons (cycled to peak temperatures in the range 400°–1050°C.): grey iron; white iron; spheroidal-graphite iron.

Heat-Resisting Alloys and Steels (cycled to peak temperatures in the range 650°–1050°C.): 'Nimonic 90'; 'Nimonic 100'; 'G-42B'; 'G-39'; 'Stellite X40'; 19-9-Ti chromium-nickel stainless steel; 19 per cent. chromium iron.

Compositions and heat-treatments are tabulated, and the factors influencing thermal-fatigue life, and the validity of applying test results to service problems, are discussed.

Consideration of the test data obtained leads the authors to draw the following conclusions:

'1. In general, the alloys with the greatest hot strength give the greatest resistance to cracking, provided that the strains are not too large (and the comparison is made between alloys of similar Young's modulus and coefficient of expansion).

'2. When the thermal strains are increased, it appears, as Forrest has suggested, that ductility becomes more important than strength.

'3. In steels, any phase changes during the thermal cycle should be avoided if possible, particularly the martensite transformation, which rapidly gives rise to deep blunt-ended cracks.

'4. An annealing effect at the peak temperature may be helpful, as indicated by the improvement in life of 'Nimonic 90' when the peak temperature was high enough to allow recrystallization.

'5. In steels the cracks were usually fairly straight, with no relation between the crack path and the grain structure. In 'Nimonic 90' and 'Nimonic 100' there was a gradual change from crack initiation on slip planes to cracking at grain boundaries when the peak temperature in the cycle was increased.

'6. Two heat-resisting alloys in the cast condition ('G-39' and 'Stellite X40') showed thermal-fatigue cracks which travelled through interdendritic constituents. This suggests that the relatively poor behaviour of these alloys, compared with the wrought heat-resisting alloys, may be attributed to their heterogeneity.

'7. The angle between the axis of the test piece and the direction of working had no detectable effect on the rate of cracking in specimens cut from a chromium-molybdenum-steel forging. However, earlier tests on bar showed that a directional effect can be found when the amount of reduction in hot working has been large.

'8. Brittleness at high temperatures is not expected to affect the life, because the surface is then in compression. (In contrast, the thermal conditions used by Glenny and Taylor* are capable of producing tension at the peak temperature, and a tendency to hot-shortness may then seriously reduce the life.)

'9. Since tension can build up to a high stress level during cooling, it would be expected in the present tests that brittleness at the minimum temperature in the cycle would lead to rapid cracking. Such behaviour has been found in some varieties of cast iron and in one of the steels (a 1·2 per cent. carbon steel). Some of the other steels which have high fracture-transition temperatures might well crack more readily in large components than they do in these small test pieces.

'10. A greater improvement in life can be obtained by reducing the peak temperature in the cycle than by a corresponding increase in the minimum temperature; but alloys which are brittle at low temperatures may provide an exception to this rule.

'11. The effect of a sharp notch in the surface is to initiate cracking at or near to the beginning of thermal cycling, thereafter the rate of growth of the crack is not greatly affected by the notch.

* See abstract in *Nickel Bulletin*, 1960, vol. 33, No. 10, pp. 250-1.

'12. Notch depth is not very critical, since depths of 0·002–0·020 in. (0·05–0·5 mm.) appeared to be equally effective. However, a very deep notch which penetrates the heated layer provides local stress relief and retards or inhibits cracking.

'13. Multiple notches have less effect on the initial rate of crack growth than a single notch, provided that the spacing between notches is less than some critical distance. Similarly, adjacent cracks propagate less rapidly than an isolated crack.

'14. When the peak temperature in the thermal cycle is reduced, a stage is eventually reached where crack initiation becomes more difficult than propagation and the numbers of cracks decrease. In general, notch sensitivity would be expected to be at its greatest at this stage, and the results tend to confirm this.

'15. None of the alloys tested could be said to be the best under all the conditions used. With peak temperatures in the range 850°–1050°C. an austenitic stainless steel and a 19 per cent. chromium iron gave the best lives. Of these two alloys, the austenitic steel showed less surface distortion but was much more notch sensitive.

When the peak temperature was below 800°C., 'Nimonic 100' gave the longest life, followed by a silicon-chromium valve steel, which was overtaken below 700°C. by a tungsten-chromium die steel and 'Nimonic 90'.

'16. Good examples of nodular cast iron approached the plain-carbon steels in resistance to cracking. With high peak temperatures nodular iron gave its best life in the annealed (ferritic) condition. The as-cast (pearlitic) condition tended to be slightly better at lower temperatures.

A sample of white cast iron broke in the first cycle of 20°–600°C., but withstood a mild cycle such as 40°–400°C. A grey engineering cast iron provided intermediate behaviour between the white and nodular irons.

'17. The results of these thermal-fatigue tests cannot in general be applied to service conditions where the time-temperature-strain cycle is considerably different. The degree of restraint requires special attention, and also the direction of restraint. Restraint in two directions results in biaxial stresses and increased strains compared with a uniaxial system. Another vital factor is the type of thermal cycle (*see* conclusion 8); there are four basic types, and important differences exist in the temperature-strain sequence.'

Properties of Stainless-Steel Sandwich Structures

H. SMALLEN and W. F. ROBERTS: 'Properties of Stainless-Steel Sandwich Using Low-Density Honeycomb Cores.'

Welding Jnl., 1961, vol. 40, Feb., pp. 90s–6s.

The test programme described was initiated to determine the mechanical properties of stainless-steel sandwich structures varying in nominal honeycomb-core density from 2·0 to 7·5 lb./cu. ft.: more generally, the authors wished to obtain an indication of the limitations and potentiality of low-density honeycomb cores from the standpoint of fabrication and design.

'17-7 P.H.' steel was used for the core, and 'P.H. 15-7 Mo' for the facing. The panels were fabricated using a sterling silver-lithium brazing alloy, and then heat-treated to the TH1050 condition. The data presented were derived from: (1) tension and compression tests on facing sheets; (2) flatwise-tension, flatwise-compression and edgewise-compression tests on sandwich specimens; (3) determination of the elastic modulus and shear modulus of the core.

'RA-333': High-Temperature Alloy Suitable for Critical Parts in Heat-Treating Furnaces

J. MAXSON: 'A New High-Temperature Alloy.'

Metal Progress, 1961, vol. 79, Feb., pp. 97–100.

'RA-333', the development, properties and commercial potentiality of which form the subjects of the present article, was developed to satisfy demands for improved materials for muffles, retorts, radiant tubes, fixture and related furnace parts. The specific requirements were: good strength at temperatures over 1800°F. (980°C.); adequate resistance to oxidizing, carburizing, nitriding and other atmospheres; and reasonable fabricability. Cost and availability were also given due consideration.

The factors and research which culminated in the evaluation of the final composition* are discussed. Short-time tensile and stress-rupture properties exhibited by test specimens machined from 1-in. (2·5 cm.) bar produced during laboratory studies are tabulated.

Subsequent tests on the first large heat produced showed the alloy to have excellent oxidation-resistance and good resistance to thermal fatigue. Its coefficient of thermal expansion was established as $8{\cdot}85 \times 10^{-6}$ in the range 70°–1800°F. (20°–980°C.). Limited creep tests at 2200°F. (1205°C.) gave promising results.

Although the alloy was designed for use at temperatures higher than 1800°F. (980°C.) (e.g., in high-temperature carburizing furnaces and brazing processes), such applications have proved less extensive than first thought. Interest has, however, been shown in its suitability for baskets, fixtures and radiant tubes in carbo-nitriding and carburizing furnaces and for other conventional applications. In addition to in-process and standard metallurgical testing for the heat-treating industry, the alloy is also undergoing evaluation by the glass industry.

Nickel-containing Spring Alloys for Special Applications

H. HOLETZKO: 'Nickel-containing Spring Alloys.'

Maschinenmarkt, 1960, vol. 66, July 29, pp. 15–18.

Nearly 90 per cent. of all the springs employed in industry are fabricated from unalloyed or low-alloy

* Nickel 45, chromium 25, tungsten 3, molybdenum 3, cobalt 3, silicon 1·25, carbon 0·08 max., per cent. Harmful residuals are carefully restricted, and, in general, limited to 0·03 per cent.

Output of Stainless Steel (Including Heat-Resistant Grades) in Main Producing Countries
(Compiled by *Metal Bulletin* from official statistics: *see abstract on p. 130*)

Country	1955	1956	1957	1958	1959	1960
Ingots ('000 *tons*)						
U.S.A. (short)	1222·3	1225·7	1046·9	895·6	1126·8	1004
W. Germany (metric) ..	132·4	128·5	125·4	136·2	191·4π	259·4π
U.K. (long)	134·7	141·2	165·4	148·4	168·1	219·9
Japan* (metric)	29·5	53·1	59·4	61·2	102·3	178·3
France† (metric)	73·8	84·8	99·2	96·7	123·4	190·0‡
Sweden (metric)	83·8	94·8	103·0	108·4	142·2	176·5
Italy† (metric)	19·6	28·0	25·6	35·6	44·6	58·4§
Castings (not included above)						
U.S.A. (short)	4·1	7·4	3·2	2·6	2·4	n.a.
W. Germany (metric) ..	19·0	20·7	19·3	21·2	22·2π	28·8*p*π
U.K. (long)	23·4	26·3	24·4	22·8	23·9	26·5
Sweden (metric)	2·5	2·6	3·0	2·5	3·2*e*	3·6*e*

* Hot-rolled products. † Includes castings or steel for castings. ‡ Including *c.* 5000 tons castings, 1/2000 tons of castings made by non-members of CSPAFS. § Ingots only. Production of steel for castings 4200 tons. π Including Saar. n.a. Not available. *p* Provisional. *e* Estimated.

spring steels. As materials of construction for the remaining 10 per cent. (which are employed in applications requiring special characteristics) use is usually made of the chromium-nickel stainless steels and such non-ferrous alloys as those of copper or nickel base. In this respect, the nickel-base alloys can offer technical and economic advantages when: (a) the springs are subjected to operating temperatures above 180°C. or considerably below 0°C.; (b) the spring is exposed to severely corrosive media (as in the oil-refining or process industries); (c) non-magnetic characteristics are required over a wide range of temperature (even below 0°C.); (d) a constant modulus of elasticity is required over a wide temperature range.

In this paper the author first outlines the characteristic features of the nickel-base alloys as a class (corrosion-resistance, oxidation-resistance, mechanical and elastic properties, fatigue properties, and relaxation characteristics are commented upon), and then discusses data presented in illustration of the advantages offered by alloys comprising the four types employed for springs: (1) age-hardenable alloys containing 93–98 per cent. nickel; (2) nickel-copper alloys; (3) nickel-chromium-base alloys; (4) nickel-iron-base alloys.

Experience in Forging 'Astroloy'

J. LUCHOK: 'How to Forge 'Astroloy'.
Metal Progress, 1961, vol. 79, Feb., pp. 91–3.

The nickel-base alloy 'Astroloy'*, one of the newest 'superalloys', exhibits very good tensile and stress-rupture properties, particularly at temperatures higher than 1400°F. (760°C.). Heat-treatments developed for 'Astroloy' sheet, and the properties obtainable in sheet and in investment castings, have been previously reported by BARKER *et al.*: see abstract in *Nickel Bulletin*, 1961, vol. 34, No. 2, p. 44. On the assumption that the alloy could prove useful for turbine wheels or discs in jet or missile engines where other nickel-base alloys of similar type would be of marginal applicability or unusable, engineers of Wyman-Gordon Company undertook work to evolve the necessary techniques for forging 'Astroloy'. The scope of this work and the results obtained to date are outlined in the present article.

Exploratory work carried out to determine the effect of forging temperatures in the range 1850°–2100°F. (1010°–1150°C.) on small vacuum-cast billets revealed the optimum forging temperature to fall in the range 2075°–2125°F. (1130°–1165°C.). To minimize heat loss during forging (which could result in surface rupturing), it was found essential to keep the transfer time from furnace to forging to the absolute minimum (and best results were obtained when the time interval was less than 20 seconds.). The Company is now able to produce large forgings (up to 1,000 lb. (454 kg.) in weight and 35 in. (89 cm.) in diameter): data indicating the minimum tensile properties obtainable in such forgings at room temperature and 1400°F. (760°C.) are included in the paper. Stress-rupture properties at 1800°F. (980°C.) are also given.

Work on heat-treatments to improve mechanical properties, and investigations to increase the variety of shapes producible by forging, are continuing.

* Nominal composition: chromium 15, cobalt 15, molybdenum 5, aluminium 4·5, titanium 3·5, carbon 0·5, silicon 0·05, manganese 0·05, boron 0·03, per cent., remainder nickel.

Stainless-Steel Production in 1960

'Stainless Steel Reviewed.'

Metal Bulletin, 1961, Mar. 7, pp. 11–13.

In this short article, data available on stainless-steel production in the U.K. during 1960 are summarized, output figures for the main British stainless-steel-producing companies are estimated, and consumption by various industries is commented upon. Details of schemes undertaken by various U.K. firms to improve or extend production or fabricating facilities are included in the survey. Tonnages of stainless steel exported to various countries in 1957, 1958, and 1959 are listed, new outlets are discussed, and finally the competition anticipated from other stainless-steel-producing countries is alluded to.

A table summarizing stainless-steel output in various countries during the years 1955–1960 is reproduced on p. 129.

Experiences in the Continuous Casting of Stainless Steel

B. MATUSCHKA: 'Production of Stainless Slabs at the Continuous-Casting Plant of Schoeller-Bleckmann Stahlwerke A.G.'

Jnl. Iron and Steel Inst., 1961, vol. 197, Mar., pp. 189–98.

In this paper the author outlines experience with a continuous-casting plant (based on the Rossi system and intended mainly for the production of austenitic stainless-steel slabs) installed by Schoeller-Bleckmann Stahlwerke A.G.

No difficulties were encountered in casting the unstabilized grades of stainless steel to which the process was first applied, and, subsequently, in November 1958, titanium-stabilized types were introduced into the casting programme. Although the Company is now successfully casting titanium-stabilized steels (with or without molybdenum) in weights up to 18 tons, it was early found that success in casting a particular type of steel depended upon the development of an appropriate casting procedure. After giving details of the plant and basic casting process, the author therefore draws attention to the modifications necessitated in casting titanium-stabilized steels, and finally comments upon the quality of the continuously-cast steels produced and the types of defect which are liable to be encountered.

Morphology of Martensite in Nickel-containing Steels

P. M. KELLY and J. NUTTING: 'The Morphology of Martensite.'

Jnl. Iron and Steel Inst., 1961, vol. 197, Mar., pp. 199–211.

In the investigation described, the authors, using the thin-foil technique and transmission electron microscopy, studied martensite formation in plain-carbon steels (carbon 0·1–1·4 per cent.), 0·8 per cent. carbon-20 per cent. nickel steel, and 18–8-type stainless steel.

The results presented show that two distinct types of martensite may be produced on quenching. In high-carbon steel and in the 20 per cent. nickel-0·8 per cent. carbon steel, the transformation product consists of plate-like grains of martensite, which are internally twinned on a fine scale. Detection of these fine twins, together with the crystallographic data obtained from the thin foils, provided experimental verification of certain assumptions made in recent phenomenological theories of martensite formation. In low-carbon steels and in the 18–8 stainless steel, the martensite was in the form of laths or needles, with no trace of internal twinning. The authors propose a transformation mechanism applicable to this type of martensite (which is not treated by current theories).

The variation in morphology and substructure of the martensite produced in different steels is used to explain certain aspects of the mechanical properties of martensite and its behaviour during the early stages of tempering. The factors governing this change in morphology are discussed, and some evidence for the mechanism of the stabilization of austenite is presented.

1st International Congress on Metallic Corrosion

The First International Congress on Metallic Corrosion was held in London, April 10–15, 1961. The eighty-two papers presented at the Congress (available to us under one cover in preprint form) are shortly to be published by Butterworths, London, together with the discussions to which they gave rise. Due reference will be made to this monograph when it is published. Considerations of space not only preclude inclusion of abstracts of papers of no specific relationship to nickel or nickel-containing materials (papers of indirect or fundamental interest are, however, noted), but also, in the main, restrict the abstracts which are included to a brief indication of the scope of the information covered. The abstracts are listed under the headings of the sections in which they were presented at the Conference.

Inhibitors

E. UUSITALO: 'Establishing the Effect of Corrosion Inhibitors by Potential and Polarization Measurements with Particular Reference to Operative Equipment', pp. 232–7.

D. M. BRASHER: 'The Zero Charge Potential of Metals in Relation to the Inhibition of Corrosion', pp. 56–8.

L. I. ANTROPOV: 'Inhibitors of Metallic Corrosion and the *phi*-Scale of Potentials', pp. 317–25.

N. HACKERMAN and R. M. HURD: 'Corrosion Inhibition and Molecular Structure', pp. 313–6.

Fundamental Studies

D. A. VERMILYEA: 'What I'd Like to Know about Corrosion', pp. 34–43.

Corrosion is discussed from the point of view of the atomic processes involved.

C. EDELEANU and J. G. GIBSON: 'Influence of Crystal Structure on Corrosion', pp. 59–63.

M. WYN ROBERTS: 'Factors which may Influence the Initial Reaction of Gases with Metals', pp. 238–42.

The article is confined to a discussion of the initial stages of the interaction of gases with metals. Fundamental aspects of gas/metal reactions are reviewed, recent investigations on specific metal/gas systems (e.g., calcium/nitrogen, calcium/oxygen, iron/oxygen, and nickel/hydrogen sulphide) are considered, and the salient mechanistic features are discussed.

R. LITTLEWOOD and E. J. ARGENT: 'Corrosion in Fused Chlorides', pp. 379–82.

From thermodynamic analysis of the factors determining corrosion in a given metal/molten-chloride system, it is concluded that the nobility of the metal and the stability of the chloride melt are of primary influence. Study of the electrode-potential behaviour of nickel in an alkali chloride melt showed that the Redox potential of a fresh melt is initially much higher than the potential of the metal and that they gradually approach each other until the metal becomes immune, when corrosion ceases. The rate at which this occurs depends on the impurity content of the melt and the ratio surface-area-of-metal/volume-of-melt. The safest way of avoiding corrosion in fused chlorides, particularly with the relatively noble metals iron and nickel, is regarded as the attainment of immunity.

N. D. GREENE: 'The Passivity of Nickel and Nickel-base Alloys', pp. 166–70.

The active/passive transitions of nickel and nickel-base alloys ('Hastelloy B', 'Hastelloy C', 'Hastelloy F', and various nickel-molybdenum and nickel-tungsten alloys) in sulphuric acid and hydrochloric acid were studied using potentiostatic anodic-polarization techniques. Account was taken of the effects of temperature and acid concentration. The results presented suggest that nickel and its alloys offer promise, under certain conditions, as corrosion-resisting materials for use in oxidizing environments, and that anodic-protection techniques may extend their utility in both hydrochloric and sulphuric acids.

U. F. FRANCK: 'Electrochemical Studies of Pitting Corrosion of Passive Metals', pp. 197–200.

T. ISHIKAWA and G. OKAMOTO: 'On the Electrochemical Study of Austenitic Stainless Steel in Sulphuric Acid Containing Various Kinds of Oxidizing Agents', pp. 444–8.

The authors discuss the results of experiments in which the polarization characteristics of austenitic stainless steel in sulphuric acid were studied (using potentiostatic and galvanostatic techniques) as a function of the nature of the oxidizing agents present (e.g., oxygen, hydrogen peroxide, ceric, mercuric, ferric, cupric, chromate, vanadate, molybdate, permanganate, persulphate, periodate and other ions).

Cathodic and Electrolytic Protection

D. A. SHOCK, J. D. SUDBURY and O. L. RIGGS: 'Use of Anodic Passivation for Corrosion Mitigation of Iron and Alloy Steels', pp. 144–8.

Edeleanu has pointed out that corrosion control could be established in normally corrosive acids by maintaining a steel at the passive potential. The present paper reviews research initiated to this end, and outlines recent developments in the commerical application of anodic passivation to corrosion control. The results of previous work were summarized in three papers abstracted in *Nickel Bulletin*, 1960, vol. 33, No. 5, pp. 125–7: the authors discuss the extension of the engineering experience previously reported, the effects of halogen concentration, and tests on stress corrosion.

Practical Experience

J. C. HUDSON: 'Future Corrosion Research on Ferrous Metals', pp. 281–4.

The author considers the present state of research on corrosion of ferrous metals and makes some suggestions for future work. Points discussed include the development of rust-resisting materials and improved protective coatings, research on paints and study of the composition and properties of rust itself.

M. G. FONTANA: 'Some Unusual Corrosion Problems in the Chemical Process Industries', pp. 13–17.

The author presents case-histories of failures in chemical-process plant which have proved 'costly, unexpected and/or difficult to explain', and discusses their relation to current laboratory work. Stress-corrosion failures in stainless steels are the main subject of consideration, but instances of galvanic, intergranular, pitting and fluoride corrosion are also discussed.

H. G. GEERLINGS and J. C. JONGEBREUR: 'Corrosion in Oil-Refinery Equipment', pp. 362–71.

The authors discuss corrosion in oil-refinery processing units in terms of the effects of the various compounds present in the crude oil itself or the chemicals introduced during the processing of the oil. The information is restricted to corrosion on the oil side of the equipment.

The influence of the following are considered: hydrogen chloride, naphthenic acids, sulphur and sulphur compounds, hydrogen, hydrogen sulphide + hydrogen, sulphuric acid, sulphur dioxide, phosphoric acid, caustic soda and furfural. Materials for which corrosion experience is reviewed include: austenitic nickel-chromium and nickel-chromium-molybdenum stainless steels, 'Durimet 20', and 'Hastelloy' alloys.

V. ČÍHAL: 'Corrosion Mechanisms in Ammonia Synthesis Equipment', pp. 486–90.

The author outlines the factors governing selection of materials of construction for the internal parts of ammonia converters (i.e., for applications involving exposure to nitrogen, hydrogen and ammonia at high pressure and high temperatures). Resistance both to hydrogen attack and to nitriding is considered essential.

Resistance to corrosion by hydrogen is shown to depend on the nature of the carbides present in the steel. Chromium-molybdenum steels form carbides resistant to hydrogen, but suffer severe nitriding, which appears to render them liable to attack by hydrogen. Austenitic stainless steels are regarded as the most suitable materials for such applications.

G. G. PAGE: 'Some Operating Conditions Influencing Attack of Non-Ferrous Tubular Condenser and Heat-Exchange Equipment', pp. 373–8.

Details are given of three unusual forms of inlet impingement attack (Slot, Star and Crescent), and reference is made to examples of other similar interesting forms of attack. The paper is based on observations made both in the field and in the laboratory, and the investigations are stated to have revealed several factors, not previously reported, which can effect corrosion in heat exchangers.

T. H. ROGERS: 'Practical Corrosion Problems in the Royal Canadian Navy', pp. 421–5.

The paper includes notes on, *inter alia:* corrosion in boilers, superheaters and evaporators; cathodic protection for ship's hulls; condenser materials (including reference to the satisfactory performance of iron-modified 70–30 cupro-nickel tubes); and experience with lower-nickel copper-nickel-iron alloys.

C. BRECKON and P. T. GILBERT: 'Corrosion of Condenser Tubes under Conditions of Local High Temperature', pp. 87–92.

Case histories are presented in illustration of the abnormally rapid pitting corrosion to which the interior of condenser tubes in service in oil refineries or on board ship were found to be subject due to the effects of local high temperatures on the outside of the tubes.

An apparatus designed to investigate this effect in the laboratory is described, and test data are recorded for a number of condenser-tube materials, including 70–30 and 90–10 cupro-nickels, aluminium brass, 'Admiralty brass' and 'Yorcoron' (copper-base alloy containing 30 per cent. nickel, 2 per cent. iron, and 2 per cent. manganese).

R. S. BEM and H. S. CAMPBELL: 'Laboratory Hot-Spot-Corrosion Tests of Condenser-Tube Alloys', pp. 426–30.

The results presented reveal 90–10 cupro-nickel to be less sensitive to hot-spot corrosion than 70–30 cupro-nickel; aluminium brass was affected even less. The severity of attack was greatly increased by addition of hydrogen sulphide to the sea water used for the tests (simulating polluted estuary waters), and, in polluted water, attack was considerably more severe at a hot-spot temperature of 100°C. than at 75°C., but further increase in temperature had little effect. The attack is regarded as due in part to the high temperature *per se*, but, at least in the case of 70–30 cupro-nickel in polluted water, is greatly increased by the existence of a temperature difference between the hot-spot and the surrounding cooler metal.

G. J. EVANS and H. G. MASTERSON: 'The Corrosion of Cupro-Nickel Feed-Water-Heater Tubes in C.E.G.B. Stations', pp. 440–3.

In this paper the authors outline the operating conditions under which an exfoliating type of corrosion occurred on the steam side of cupro-nickel feed-water-heater tubes in a number of Central Electricity Generating Board Stations. The results of metallurgical examinations and chemical analyses of affected tubes, and of corrosion products, are presented, and possible mechanisms of attack are discussed.

H. G. COLE: 'Corrosion and Protection of Aircraft', pp. 248–51.

Methods of protecting high-strength magnesium alloys, aluminium alloys, titanium, steel and stainless steel against corrosion, stress corrosion and corrosion fatigue are discussed, with particular emphasis on the effects of the protective treatments on the strengths of the metals.

M. H. TIKKANEN: 'Investigation of Corrosion Causes', pp. 383–7.

The author reports Finnish experience in investigation of corrosion failures, and, in illustration of the value of metallurgical examination, alludes to cases of corrosion of, *inter alia*, a welded 18–8-steel flange used in a sulphite-pulp mill, a ship-propeller bolt in 18–8 steel, an 18–8 stainless-steel tube exposed to an atmosphere of hydrogen, nitrogen and ammonia, and 25–20 chromium-nickel steel in a flowing silicate melt.

Corrosion in Atomic Energy

D. F. MacLENNAN, A. F. McMILLAN and J. H. GREENBLATT: 'The Corrosion of Aluminium and Aluminium Alloys in High-Temperature Water', pp. 306–12.

Previous ideas on the mechanism of corrosion of aluminium in high-temperature pure water are reviewed, and information obtained by optical- and electron-microscopical examination of the oxide film formed on commercial 2S aluminium and two corrosion-resistant aluminium alloys containing iron and nickel is presented. This information, together with the results of polarization studies of 2S specimens corroding in stainless-steel autoclaves, indicates that the corrosion-resistance of the iron- and nickel-containing alloys is explicable by an electrochemical mechanism, and that, in the early stages of corrosion, the previously postulated hydrogen-damage mechanism of Draley, or the stress-cracking mechanism of Tragert, are unimportant. The function of the alloying elements is considered.

W. T. EDWARDS: 'Aqueous Corrosion in the Atomic Energy Industry', pp. 509–20.

The author reviews work by the United Kingdom Atomic Energy Authority on the corrosion behaviour of materials of construction for chemical plant handling (1) nitric acid in the dissolution of nuclear fuels and the processing of slags, and (2) hydrofluoric acid in the production of uranium tetrafluoride. The data presented relate mainly to the stabilized grades of chromium-nickel stainless steel and to various nickel-base alloys.

In processes involving the use of fluoride and nitric acid, stainless steel is not considered a suitable constructional material under boiling or near-boiling conditions. Of the alternative materials investigated, tantalum, titanium and a 65-35 nickel-chromium alloy showed most promise (but even these are not entirely satisfactory, and their use is restricted to applications where fluoride concentrations are low and temperatures are below boiling point).

For plant handling hydrofluoric acid, 'Monel' is deemed the most convenient material of construction, and its performance is satisfactory provided that oxygen levels are maintained at low values (<1000 p.p.m.) in the blanket gas. An investigation of welding methods revealed that those based on the '140 Monel' electrode are undesirable, and that multiple welds are to be avoided. Although 'Monel' is not particularly susceptible to stress corrosion, it is recommended that all components should be stress-relieved where possible.

Intragranular and Stress Corrosion

D. VAN ROOYEN: 'Some Aspects of Stress-Corrosion Cracking in Austenitic Stainless Steels', pp. 134–43.

In the investigation reported, wire specimens of Type 304 18-8 steel and vacuum-melted, air-melted or levitation-melted stainless steels of basic 16-14 and 16-20 chromium-nickel type were subjected to stress-corrosion tests (under direct tensile load) in boiling 42 per cent. magnesium-chloride solution. The corrosion behaviour of the 16-20 steels was evaluated as a function of carbon, manganese, molybdenum and nitrogen contents; the 16-14 chromium-nickel steels were tested at various levels of carbon, titanium, manganese, silicon, aluminium, nitrogen, platinum, tin and niobium. Supplementary tests were carried out on specimens of 'A nickel', titanium-containing nickel, a nickel-copper alloy and two nickel-chromium-iron-base alloys.

The nickel and nickel-base-alloy specimens were found to be immune to cracking under the test conditions (500 hours at a stress level of 35,000 p.s.i.). Comparison of the results obtained with the 18-8, 16-14 and 16-20 steels indicated a gradual increase in resistance to stress-corrosion cracking with increase in nickel content: at these levels, however, nickel content alone is not considered to ensure any specific degree of resistance, since the presence of minor elements is also of significance.

Addition of small amounts of nitrogen, or larger amounts of molybdenum, was found to reduce the resistance of the austenitic stainless steels to transgranular stress-corrosion cracking. Increase in the carbon or nickel contents, and perhaps to a certain extent in the tin, rendered the steels more resistant to cracking. The variations in time-to-failure are attributed to differences in the reaction time preceding crack propagation, the rate of crack penetration remaining approximately constant.

The results of tests on composite stress-corrosion specimens comprising selected test materials bonded to a steel susceptible to cracking showed good correlation between the times-to-failure of the experimental materials when tested alone and the number of propagating cracks which will penetrate into them. It is suggested that crack initiation possibly comprises a form of corrosion attack (which is required to expose a path of rapid corrosion, after which true cracking proceeds).

Potential measurements indicated that strain-induced anodic depolarization cannot account for cracking entirely on the basis of an electrochemical mechanism. Preference is given to an electrochemical mechanism wherein reaction takes place at sites of structural and compositional changes in the steels. These may be formed under the influence of stress, setting up paths of easy localized corrosion.

R. E. REED and H. W. PAXTON: 'Stress-Corrosion Cracking of Single Crystals of Some Austenitic Stainless Steels', pp. 267–74.

Investigation of stress-corrosion cracking in polycrystalline materials is handicapped by the difficulties involved in the identification of the crystallography of the process. In the experiments described, this difficulty was overcome by using single crystals to study the crack-nucleation site, the orientation of the crack plane, the fracture-time/stress relationship, the fracture-surface morphology and the corrosion-product composition during stress-corrosion cracking of austenitic stainless steels.

Single crystals of three materials (Fe-20Cr-20Ni and Fe-20Cr-12Ni alloys and commercial Type 304 18-8 stainless steel) were loaded in tension in boiling 42 per cent magnesium-chloride solution. Type 304 stainless steel cracked or fractured in 4-17 hours, the Fe-20Cr-12Ni alloy in 16-62 hours, and the Fe-20Cr-20Ni in 70-170 hours: the crack in all three materials nucleated from elongated pits formed when portions of slip lines were attacked by the solution. The crack plane of the Fe-20Cr-20Ni specimens followed the (100) plane with the highest normal stress upon it (this is believed to be the first time that brittle cracks have been observed to follow a particular crystallographic plane in face-centred-cubic material). Electron-diffraction patterns made of the corrosion product from an Fe-20Cr-20Ni crack face suggested that it may be a chromium-iron oxide. Colorimetric analysis of the corrosion solution revealed an increase in nickel during the test.

The general crack plane in Type 304 and Fe-20Cr-12Ni specimens was found to be approximately normal to the tensile axis, and electron micrographs of the fracture surface on a Type 304 specimen revealed possible crystallographic steps on a small scale.

It is proposed that the mechanism underlying this process probably comprises two stages: (1) a slow electrochemical crack-initiation and re-initiation step, and (2) a rapid mechanical-fracture step.

I. G. MURGULESCU and O. RADOVICI: 'The Potentiostatic Behaviour of some Cr-Ni-Mn Stainless Steels', pp. 302-5.

The authors report a potentiostatic study of the behaviour of three chromium-nickel-manganese-titanium steels in 1 *N* sulphuric acid. Values established for Flade potential, maximum current before establishment of passivity (critical current), and the dissolution current of the passive metal film were found to be influenced by steel composition and by solution temperature. Secondary passivation was observed.

H. R. COPSON: 'Effect of Nickel Content on the Resistance to Stress-Corrosion Cracking of Iron-Nickel-Chromium Alloys in Chloride Environments', pp. 112-17.

There is some evidence in the literature that the resistance of austenitic stainless steels to stress-corrosion cracking increases with increase in nickel content. The validity of these findings has been investigated in laboratory tests (on alloys ranging in nickel content from 8 to 77 per cent.), the preliminary results of which have been previously published by the author (and were referred to in *Nickel Bulletin*, 1960, vol. 33, No. 5, pp. 123-4). Recent results obtained on annealed wire are given in this paper. The data presented support the conclusion that iron-nickel-chromium alloys containing more than 45-50 per cent. nickel, 15-24 per cent. chromium, balance mainly iron, are immune to cracking in the boiling 42 per cent. magnesium-chloride test solution.

The good performance of the high-nickel alloys in the laboratory tests described has been confirmed by experience with commercial alloys: in this connexion, the author presents the results of field tests (using small disc-shaped specimens of nickel, 'Monel', 'Inconel', 'Hastelloy F', 'Ni-O-Nel', 'Carpenter 20' and various grades of austenitic stainless steel), and of actual service tests on equipment in the same materials. In these tests 'Inconel' (nominal composition about 75 per cent. nickel, 15 per cent. chromium, 7 per cent. iron) resisted cracking in chloride-containing environments which induced failure in austenitic stainless steels.

Since the stainless steels may crack also in other environments, the author comments on data available on the corrosion behaviour of 'Inconel' (selected as a typical high-nickel alloy) during exposure to molten metals, nitric acid, caustic solutions and high-pressure hydrogen. It is emphasized that, in considering 'Inconel' or any other alloy for use in a new environment, it is logical first to carry out stress-corrosion-cracking tests.

E. H. PHELPS and R. B. MEARS: 'The Effect of Composition and Structure of Stainless Steels upon Resistance to Stress-Corrosion Cracking', pp. 157-65.

In the light of the marked differences reported in the stress-corrosion behaviour of the austenitic stainless steels and the martensitic stainless steels (e.g., when treated to very high strength levels), the authors undertook the investigation now described with the aim of comparing the stress-corrosion behaviour of representative martensitic and austenitic stainless steels in a number of corrosive environments. The influence of anodic and cathodic polarization on stress-corrosion behaviour was also studied.

The stress-corrosion tests were carried out on two chromium martensitic steels (A.I.S.I. Type 410 and 'U.S.S. 12MoV') and two chromium-nickel austenitic steels (Types 302 and 304) during exposure to the following solutions: 3 per cent. NaCl aerated with oxygen; 10 per cent. NaCl containing H_2O_2; 10 per cent. $FeCl_3$; boiling 42 per cent. $MgCl_2$; 3 per cent. NaCl + 0·5 per cent. acetic acid; 3 per cent. NaCl + H_2S; 3 per cent. NaCl + 0·5 per cent. acetic acid + H_2S.

The high-strength '12MoV' stainless steel was found to be susceptible to stress-corrosion cracking at room temperature in several solutions containing anions other than chloride; comparative tests on Type 410 steel in the tempered condition, and Type 304 in the annealed condition, showed them to be resistant to cracking. '12MoV' was also susceptible to cracking in a series of solutions containing chlorides, and, except in solutions containing sulphide, Type 410 was substantially more resistant to stress corrosion.

With the exception of boiling 42 per cent. magnesium-chloride solution, Types 302 and 304 steels in the annealed condition did not prove susceptible to stress corrosion in any of the solutions. In the highly cold-worked condition, however, the same steels were found to be subject to attack in some of the chloride solutions at room temperature.

Cracks in the austenitic stainless steels were transgranular, while cracking in the martensite steels could, it was shown, be either inter- or transgranular, depending on the environment.

Polarization experiments indicated that stress corrosion of cold-worked Type 302 stainless steel in 3 per cent. NaCl saturated with H_2S was caused by corrosion along an active path. The data indicate that at high cathodic current densities cracking is attributable to a hydrogen-embrittlement mechanism. In the case of Type 410 stainless steel exposed, in the tempered condition, to the same environment, neither anodic nor cathodic polarization had any appreciable effect on time-to-failure.

Experimental Methods and Laboratory Corrosion Testing

P. C. S. HAYFIELD: 'The Drude-Tronstad Polarimeter and its Use in Corrosion Studies', pp. 212–18.

The polarized-light method of examining films on metals is described, and its application to corrosion studies is critically assessed.

W. D. MCMASTER: 'The Accelerated-Corrosion Testing of Metals', pp. 118–23.

The author reviews the advantages and limitations of the following accelerated-corrosion tests: the humidity test, neutral salt-spray test, acid salt-spray test, copper-accelerated acid salt-spray test, 'Corrodkote' test, General Motors cycled humidity test, sulphur-dioxide test, beaker corrosion tests, and miscellaneous procedures for evaluation of protective coatings and environments.

K. BARTON: 'Acceleration of Corrosion Tests on the Basis of Kinetic Studies of the Rate-Controlling Combination of Factors', pp. 401–6.

W. WIEDERHOLT: 'Laboratory Corrosion Testing', pp. 461–7.

The author reports work on the evolution of various corrosion-testing techniques, and comments on the German specifications covering them.

Atmospheric Corrosion

S. G. CLARKE and E. E. LONGHURST: 'The Corrosion Behaviour of Metals and Protective Coatings in Tropical Atmospheric-Exposure Tests', pp. 70–82.

The authors summarize the results of a series of atmospheric-corrosion tests carried out in tropical locations to establish the corrosion-resistance of steel and a range of non-ferrous metals and alloys, and to evaluate the protection conferred by various coating systems.

Corrosion data are presented for steel, aluminium and aluminium alloys, zinc and zinc alloys, copper, brass, aluminium-brass and a magnesium alloy. The coatings evaluated were applied by the following techniques: cadmium plating, zinc plating, sherardizing, tin-zinc plating and spraying, galvanizing, lead plating, lead-tin hot dipping, copper plating, tin plating and hot dipping, silver plating, brass plating, nickel plating, nickel + chromium plating, painting.

Corrosion of metals during atmospheric exposure at typical wet tropical sites can, it is concluded, be said to be not, on the whole, severe by comparison with the corrosion levels encountered in the U.K. On a surf-beach, corrosion (notably of steel) can be heavy, but some metals, particularly aluminium, cadmium, lead and nickel, are relatively highly resistant.

I. L. ROSENFEL'D: 'Atmospheric Corrosion of Metals: Some Questions of Theory', pp. 100–7.

The author outlines the electrochemical methods of investigation developed to study atmospheric corrosion, using thin electrolytic layers as the corrosive media.

C. P. LARRABEE and S. K. COBURN: 'The Atmospheric Corrosion of Steels as Influenced by Changes in Chemical Composition', pp. 252–60.

Since the introduction in 1933 of the copper-containing high-strength low-alloy steel 'U.S.S. Cor-Ten', the United States Steel Corporation has conducted an extensive series of atmospheric tests on hundreds of steels of different experimental compositions. The data obtained on 270 different low-alloy steels in atmospheric tests of 15·5 years' duration in industrial, semi-rural, and marine atmospheres are recorded and discussed in the present paper.

In the introductory section of the paper, test methods are described, the types and relative corrosiveness of the different atmospheres are compared, and the results of long-time exposure tests are plotted to indicate the shapes of time/corrosion curves for steels varying in corrosion-resistance.

As a means of determining their individual and combined effects, the five constituent elements studied in the 270 steels tested were systematically varied at the following percentage levels:

Chromium: residual; 0·6; 1·2.
Copper: 0·01; 0·04; 0·1; 0·2; 0·4.
Nickel: residual; 0·1.
Phosphorous: residual; 0·06; 0·1.
Silicon: residual; 0·2; 0·5.

On the basis of the corrosion data presented, it is concluded that rise in copper content from 0·01–0·04 had more effect on corrosion-resistance than the addition of a similar amount of any other element investigated: further increases in copper content were beneficial, but not to such a great extent as the smaller additions.

Corrosion-resistance was improved by relatively small single additions of nickel, chromium, silicon and phosphorus, but these elements were more effective when added in specific combinations.

The effects of each element are not, it is considered, additive, and data from long-time exposure tests on

a great number of steels are therefore necessary for rapid estimation of the corrosion-resistance of steels containing particular combinations of alloying elements.

High-Temperature Oxidation

P. HANCOCK: 'The Corrosion of Nickel-Chromium Alloys in Sulphur-containing Atmospheres at High Temperatures', pp. 290–8.

Nickel-chromium alloys of 80-20 type are used extensively in high-temperature turbine and furnace construction. For economic reasons it is, however, often necessary to run turbines and furnaces on low-grade high-sulphur fuels, a procedure which results in appreciable contamination of the operating atmospheres. The 18-20-type alloy is markedly less corrosion-resistant under these conditions, and appreciable internal sulphidation occurs. Previous investigators have found the predominant sulphide to be a chromium sulphide. The work now described was undertaken with the object of elucidating the mechanism involved in this type of attack, and, if possible, determining methods of improving the resistance of the alloys.

The investigations were carried out in five main stages, designed, respectively, to study the effects of: (1) hydrogen sulphide on nickel and chromium at 900°C.; (2) hydrogen sulphide and sulphur dioxide on an 80-20 nickel-chromium alloy; (3) cooling rate on an 80-20 alloy after corrosion in hydrogen sulphide at 900°C.; (4) chromium diffusion during sulphur attack; (5) increased chromium content on the corrosion rates of nickel-chromium alloys in hydrogen sulphide and in sulphur dioxide.

The tests were carried out at temperatures in the range 600°-900°C. The test apparatus, which enables specimens to be removed from the hot zone containing the corrosive atmosphere, without their being touched or the atmosphere's being disturbed, is described. The sulphidation conditions employed are stated to be much more severe than those normally encountered in practice.

Corrosive attack of the nickel-chromium alloys in sulphur-bearing atmospheres was markedly influenced by the composition of the alloy, the nature of the corroding atmosphere, and the temperature during exposure.

At sufficiently high chromium contents, the formation of a coherent scale of high melting point, which is, it is concluded, possible under either oxidizing or reducing conditions, gives some degree of protection to the underlying alloy. Under extremely severe conditions of sulphidation, where appreciable chromium impoverishment of the subscale is likely, alloys containing 50 or 60 per cent. chromium are more corrosion-resistant than those of lower chromium content, but where subscale impoverishment is not so pronounced, a 65-35 nickel-chromium alloy is to be preferred, in that it has the advantage of being single-phase.

Due to the formation of a surface-oxide film, sulphide attack of nickel-chromium alloys is not so severe under oxidizing conditions as under reducing conditions. In both hydrogen-sulphide and sulphur-dioxide atmospheres the severity of the attack increased with rise in temperature over the range investigated.

The data show that severe sulphur attack of the 80-20 alloy, particularly under reducing conditions, leads to the formation of an intimate mixture of both chromium sulphide (CrS) and nickel sulphide (Ni_3S_2), and, at temperatures above 645°C., the nickel sulphide can form a liquid phase which is capable of causing accelerated corrosion. After corrosion, the amount of nickel sulphide observed in the alloy is, however, governed by the rate of cooling from the test temperature.

H. LEWIS and R. A. SMITH: 'Corrosion of High-Temperature Nickel-base Alloys by Sulphate-Chloride Mixtures', pp. 326–36.

The adequate oxidation-resistance of the 'Nimonic' nickel-base high-temperature alloys has been convincingly proven by their service behaviour in aircraft gas turbines burning high-grade distillate fuel with considerable excess of air. Nevertheless, corrosion of 'Nimonic 100' blades has from time to time occurred under conditions providing some evidence of the presence of an agent capable of promoting sulphur attack in an oxidizing atmosphere. In such cases, the amount of sulphur present in the fuel was sufficient to provide only a small content of sulphur-bearing gas in the turbine atmosphere, a content which both information in the literature and short-term laboratory experiments indicated would not readily promote the extensive sulphidation-cum-oxidation effects observed.

In order to reproduce this type of attack rapidly in the laboratory, for purposes of alloy comparison and development, use has been made of a test in which alloys are half-immersed in mixtures of sodium sulphate and sodium chloride while being heated in air. Such tests, employing a mixture of sodium sulphate with 0·5 per cent. sodium chloride, were found to reproduce the relative behaviour of 'Nimonic 100' and the more resistant 'Nimonic 90' observed under service conditions. The subsequent occurence, in service, of excessive corrosion of the same type in 'Nimocast 258' (which had been resistant to the 0·5 per cent. NaCl mixture) led, during later research, to the use of a more drastic test, and a mixture of higher chloride content (25 per cent. NaCl) was employed, although no direct evidence exists of definite proportions of the respective constituents in deposits found on blades.

The present paper describes the results of tests undertaken to determine the effect of the composition of the corrosive salts on 'Incoloy DS', 'Nimonic 75', 'Nimonic 80A', 'Nimonic 90', 'Nimonic 100', 'Nimonic 105', 'Inconel X', and 'Inconel 700' at temperatures in the range 700°-1000°C. A report is also made of subsequent investigations of the effect of a number of compositional variables on the susceptibility of experimental nickel-chromium-cobalt-molybdenum-aluminium-titanium alloys to corrosion by the 0·5 per cent. NaCl and 25 per cent. NaCl mixtures at

900°C. These experimental alloys covered the compositional field in the neighbourhood of the 'Nimonic 100' and 'Nimonic 105' alloys, including modifications considered to be of possible value in developing better corrosion-resistance or creep properties. The data obtained permit assessment of the minimum alloy content (in terms of chromium, titanium and aluminium) required to give an arbitrary level of corrosion resistance in the 1-hour tests at 900°C. Account was taken of the effects of cobalt and molybdenum contents, and of additions of thorium, magnesium, copper, manganese, vanadium, zirconium, beryllium, cerium, tungsten, niobium and silicon.

The conclusions which the authors draw from the data discussed are quoted below:

'In 1-hour half-immersion tests in sodium-sulphate/sodium-chloride mixtures at 900°C., on nickel-chromium-cobalt-molybdenum alloys hardened with titanium and aluminium, an 'effective-chromium' content [given by chromium(%) + 1·1 × titanium(%) + 0·7 × aluminium(%)] of more than 17·1 per cent. is required to provide immunity from severe corrosion by a mixture containing 0·5 per cent. NaCl. To prevent attack by a mixture containing 25 per cent. NaCl, the 'effective-chromium' content must not be less than 20·4 per cent.

'Additions of niobium of up to 8 per cent. have a beneficial effect on resistance to both the 0·5 per cent. and 25 per cent. NaCl mixtures, and niobium is approximately equivalent to titanium in this respect on a weight per cent. basis.

'Variation of molybdenum content between 2·33 and 9·75 per cent., or of cobalt content between 5 and 20 per cent., had no significant effect upon these limiting values of 'effective-chromium'.

'No consistent shift of the limiting 'effective-chromium' contents was observed as a result of additions of thorium, magnesium, copper, manganese, vanadium, zirconium, beryllium, cerium or tungsten, although where the alloy content was near the marginal value, some vanadium-containing alloys were more severely attacked, and most beryllium-containing alloys were less severely attacked than would have been expected.

'The ranges of chromium, titanium and aluminium content specified for all the 'Nimonic' alloys except 'Nimonic 100' are sufficient to provide immunity from severe attack by the 0·5 per cent. NaCl mixture in alloys with about 0·3 per cent. silicon. It is possible that, in the leanest compositions within these ranges, higher silicon contents, up to the specified maximum, would induce susceptibility to corrosion by that mixture, but typical production samples having compositions near the middle of the specified ranges were not attacked.

'The ranges of chromium, titanium and aluminium content specified for 'Nimonic 80A' and 'Nimonic 90', and for the more-highly-alloyed compositions within the ranges specified for 'Nimonic 75' and 'Nimonic 105', confer resistance to severe attack by the 25 per cent. NaCl mixture at 900°C., provided that the silicon content is not higher than about 0·3 per cent. Higher silicon contents increase susceptibility to corrosion, and it was probably due to the silicon level that typical production samples of 'Nimonic 80A' and 'Nimonic 90' suffered severe attack in such conditions. In typical samples of 'Nimonic 100' and 'Nimonic 105', the alloy content was too low to resist attack by the 25 per cent. NaCl mixture in spite of the lower silicon content of these alloys.'

Influence of Alloying Additions on the Electrochemical Behaviour of Stainless Steels

H.-J. ENGELL and T. RAMCHANDRAN: 'The Influence of Alloying Elements on the Electrochemical Behaviour of Corrosion-Resisting Steels.' *Zeitsch. Physikalische Chemie*, 1960, vol. 215, No. 3–4, pp. 176–84.

In the electrochemical study reported, the corrosion behaviour of straight-chromium and chromium-nickel stainless steels in sulphuric acid was studied as a function of copper, manganese and molybdenum additions and variations in the chromium and nickel contents. Passivation potentials, passivation current densities and passive dissolution current densities were measured.

The data show that nickel, copper and molybdenum additions reduce the passivation current densities and passive dissolution current densities, and therefore increase the stability of the steels in the passive condition and their capacity for passivation. The effects of increasing the chromium content were reflected mainly in the passivation potential, but also, to a lesser degree, in the passive dissolution current density.

Corrosion Experience with Nickel-containing Materials in a Nitric-Acid Concentrator

J. B. LOWE: 'Influence of Acid and Chloride Concentrations on Corrosion in a Nitric-Acid Concentrator.' *Corrosion*, 1961, vol. 17, Mar., pp. 26–8.

The refining of uranium by solvent extraction is effected in pulse columns or similar equipment. The waste product (raffinate) from this process contains numerous metallic nitrates from which nitric acid used for dissolution of the concentrates is recovered. Sulphuric acid 'springing' and evaporation of the waste raffinate is carried out to release quantities of dilute nitric-acid vapours to the recovery system, a process which also releases chlorides which form a highly corrosive environment in the concentrator when mixed with the nitric acid. Experience in combating corrosion in a nitric-acid concentrator is discussed by the author in relation to the four main steps taken to ameliorate the problem: (1) reducing the chloride content of the feedwater to a minimum; (2) generation of ozone to oxidize the chlorides; (3) employing an electrolytic cell to remove the chlorides from the nitric acid; (4) selecting suitably corrosion-resistant materials of construction.

Chlorides were found to concentrate in that portion of the tower where the acid concentration was 20–30 per cent., and the resultant corrosion necessitated

frequent replacement of bubble caps and other components. Areas subjected to high flow velocities exhibited abnormally high corrosion rates. Corrosion tests were conducted (on 'Hastelloy C', 'Carpenter 20', 'Ni-O-Nel', 'Incoloy', 'Inconel' and various grades of stainless steel) in two media: 25-35 per cent. nitric acid containing 550 p.p.m. of chlorides, and in 30-40 per cent. nitric acid containing 800-900 p.p.m. of chlorides. The results obtained are tabulated, and the degree of corrosion at each of the 12 trays is illustrated by data on Type 304 chromium-nickel stainless steel.

The author concludes that, at chloride concentrations up to 1000 p.p.m., chloride removal by electrolysis is no more efficient or less expensive than by ozonation. Members of the 18-8 series of stainless steels suffer negligible corrosion at chloride concentrations up to 200 p.p.m., and corrosion rates are tolerable at chloride contents below 600 p.p.m. at low flow velocities. At chloride concentrations higher than 900 p.p.m., however, corrosion of 18-8 steel is excessive.

Catastrophic Oxidation of Exhaust-Valve Stainless Steels in the Presence of Lead Oxide

J. C. SAWYER: 'Catastrophic Oxidation of Stainless Steel in the Presence of Lead Oxide.'

Trans. Metallurgical Soc., A.I.M.E., 1961, vol. 221, Feb., pp. 63-7.

The literature on catastrophic oxidation, though primarily concerned with the effects of MoO_3 and V_2O_5, includes references to the fact that other metal-oxide vapours (including lead oxide) appear to promote a similar type of accelerated oxidation. This latter effect is, in the case of lead oxide, of considerable commercial importance, since it is believed to be one of the fundamental causes of exhaust-valve failure in gasoline engines. In this paper the author summarizes the results of experiments carried out to study the oxidation of exhaust-valve stainless steels in the presence of lead oxide.

The composition of the two steels selected for investigation are tabulated below.

Element	'VMS 201'	21-12
C	0·52	0·20
Cr	21·00	21·00
Mn	9·0	1·25
Ni	3·88	11·50
Si	0·25 max.	1·00
S	0·06	0·03 max.
P	0·03 max.	0·03 max.
N	0·44	0·18

Heat Treatment:
Rods—As-extruded at 2050°F. (1120°C.).
Sheet—As-rolled at 1850°F. (1010°C.).

The work was carried out in two phases:

(1) Specimens of 'VMS 201' contaminated with PbO were heated at 1700°F. (925°C.) for 50 hours to determine the effects of the presence of PbO vapours on oxidation behaviour. Supplementary tests were then run in an air atmosphere to establish the weight loss of specimens coated with various oxides (including PbO, MoO_3 and V_2O_5.)

Subsequently, to explore the hypothesis that lead-oxide corrosion at elevated temperatures is an acceleration of the normal oxidation process, a thermobalance was used to determine the weight changes of 21-12 specimens during oxidation in air and in an atmosphere contaminated with PbO vapour.

(2) On the basis of the observation that chromium exhibits good oxidation-resistance in air at 1300°F. (705°C.) by virtue of the formation of a thin film of Cr_2O_3, and to throw light on the influence of PbO on the oxidation products present on the stainless steels, a study was made of the reaction between Cr_2O_3 and PbO in air at this temperature. Since iron is also catastrophically oxidized by PbO, other experiments were undertaken to observe the effects of PbO on Fe_2O_3 at high temperatures. Similar spot tests were conducted on the oxides formed on 'VMS 201' and 21-12 stainless steels when heated in air, and work was also carried out to determine whether MoO_3 and V_2O_5 would have similar effects to PbO.

It is concluded that the presence of PbO causes an acceleration of the normal oxidation process in stainless steels similar to the effects of MoO_3 and V_2O_5, oxidation occurring at the metal/oxide interface as a result of inward diffusion of oxygen.

The reaction of PbO with Cr_2O_3 was found to result in the oxidation of Cr^{+3} to Cr^{+6} and the formation of a new compound, tentatively identified as $Pb_3Cr_2O_6$; that of PbO with Fe_2O_3 resulted in the formation of a black magnetic oxide in which all of the iron ions were in the Fe^{+3} state.

Studies of the stainless steels during oxidation in air revealed that ions of Cr^{+3}, Fe^{+2} and Fe^{+3} were present in the oxides formed. When lead oxide was present during oxidation, ions of Cr^{+6} and Fe^{+3} were found in abundance, but Fe^{+2} was absent. When the stainless steel was oxidized in the presence of MoO_3 or V_2O_5, oxidation of the chromium ion Cr^{+3} did not occur, but the absence of Fe^{+2} indicated the stabilization of the Fe^{+3} ion.

Accelerated oxidation of stainless steel in the presence of PbO is attributed to the assumption by the chromium and iron ions of the higher valency states of Cr^{+6} and Fe^{+3}, thereby preventing the formation of protective spinels.

Use of Cupro-Nickel for Fin Drums Drying Calcium-Carbonate Paste

See abstract on p. 121.

Hydrogen Pick-up During Aqueous Corrosion of Nickel-containing Zirconium Alloys

W. E. BERRY, D. E. VAUGHAN and E. L. WHITE: 'Hydrogen Pick-up During Aqueous Corrosion of Zirconium Alloys.'

Corrosion, 1961, vol. 17, Mar., pp. 109t-17t.

The use of zirconium alloys as cladding material for the fuel elements of pressurized-water reactors has induced investigation of the mechanism of hydrogen absorption by the alloys (a reaction which entails risk of embrittlement) during exposure to high-temperature water. It has been found that the amount of hydrogen absorbed in 'Zircaloy 2' ranges from 15 to 50 per cent. of that theoretically available from the corrosion reaction. Other studies have shown that nickel and platinum additions increased hydrogen absorption in zirconium under cathodic polarization during exposure to high-temperature water. The low over-voltage of nickel, and the ability of the metal to catalyze hydrogenation reactions, provided the basis for the studies now reported: sulphur and other elements are known to poison the catalytic effects of nickel in chemical reactions, and, in an attempt to achieve the same result in nickel-containing zirconium alloys, the authors undertook an investigation of the influence of various alloying additions on hydrogen absorption in such alloys during corrosion in water at 600° and 680°F. (315° and 360°C.) and in steam at 750°F. (400°C.) and 1500 p.s.i.

The data presented for a series of binary sponge-base zirconium alloys indicate that, of the alloying elements found in 'Zircaloy 2', nickel at increasing levels markedly increased hydrogen absorption. Tin has little or no effect, while iron, chromium and antimony additions reduce hydrogen absorption.

In an attempt to overcome the adverse effects of nickel, additions of arsenic, antimony, bismuth or tellurium were made to 'Zircaloy 2'. None of these elements was found to affect the amount of hydrogen absorbed during corrosion. It is postulated that, in the case of zirconium alloys containing iron, chromium or nickel, the compounds of these elements are cathodic to the zirconium matrix, and the resultant potential difference is sufficiently high anodically to polarize the zirconium and thus improve corrosion-resistance. It appears that iron and chromium compounds readily depolarize hydrogen and thereby decrease the possibility of its passage through the oxide film. Nickel compounds, it is suggested, probably do not depolarize hydrogen and may aid in its passage through the oxide film.

Heat-Treating of Stainless Steels in Protective Atmospheres

B. A. RUEDIGER: 'Heat-Treating and Sintering Stainless in an Atmosphere.'

Metal Progress, 1961, vol. 79, Feb., pp. 101-5.

In appropriate protective atmospheres stainless steels can be annealed, brazed, sintered and, in some instances, fully hardened without oxidation or discoloration. Hydrogen and dissociated ammonia are often used in protective atmospheres during bright annealing or sintering, and in this article the author discusses the characteristics of the two atmospheres and describes the various types of furnace and gas generator which may be employed.

Welding and Heat Treating a 60-ton Stainless-Steel Cryogenic Vessel

W. H. VETTER: 'Welding and Heat-Treating a 60-ton Cryogenic Vessel.'

Metal Progress, 1961, vol. 79, Feb., pp. 88-90.

This article draws attention to the factors involved in welding and heat-treating a stainless-steel vessel designed to store 8,000 gal. (36,370 l.) of liquid oxygen at a pressure of 2,000 p.s.i.

The vessel [with an inside diameter of 12 ft. 9 in. (3·8 m.)] was fabricated from A.I.S.I. Type 321 18-10 chromium-nickel-titanium stainless steel which, retaining its toughness down to −425°F. (−255°C.), is suitable for use in such low-temperature applications as the handling of liquid oxygen, nitrogen, hydrogen and helium. The gores or orange-peel segments of the shell were formed from 5-in. (12·5-cm.) thick plate under a heavy hydraulic press. In welding the spherical segments and attaching the fittings, more than 12,000 lb. (900 kg.) of weld metal was required. After welding, the entire vessel was annealed.

Arc-Welding of 'Inconel' for Nuclear-Power Applications

J. BLAND and W. A. OWCZARSKI: 'Arc Welding of a Ni-Cr-Fe ('Inconel') Alloy for Nuclear-Power Plants.'

Welding Jnl., 1961, vol. 40, Jan., pp. 22s-32s.

See abstract in *Nickel Bulletin*, 1960, vol. 33, No. 7, p. 176.

ANALYSIS

Determination of Trace Amounts of Cobalt in Nickel

See abstract on p. 117.

Attention is drawn to the fact that many of the names of materials mentioned in The Nickel Bulletin are *Trade Marks*.

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